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Design of semiconductors-based composites for the efficient photodegradation of organic micropollutants in water

Giuseppe Mele
University of Salento

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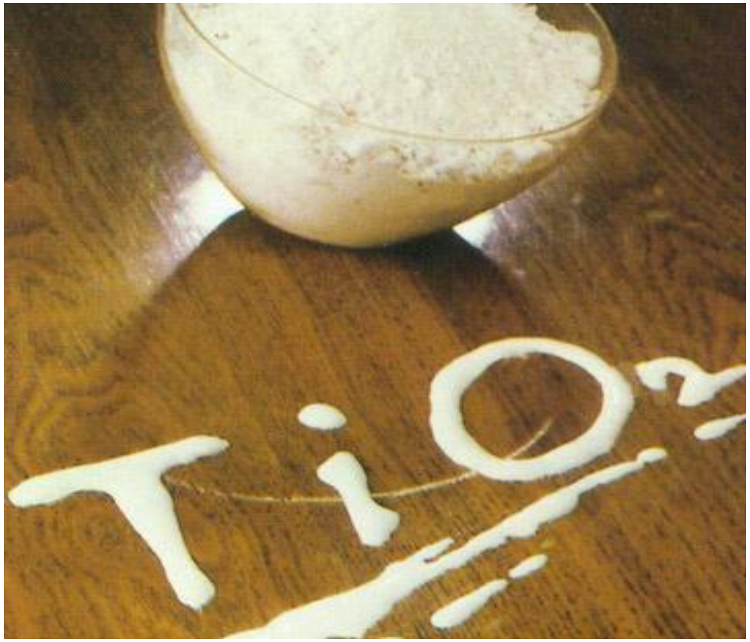
Semiconductor Materials

PHOTOCATALYSTS



Semiconductors	Bandgap Energy (eV)
CdS	2.42
ZnS	3.6
ZnO	3.436
TiO_2	3.2
SnO_2	3.54
CdS_e	1.7
Fe_2O_3	2.3
ZrO_2	3.87
Cu_2O	2.172
PbS	0.286
$LaFeO_3$	2.35

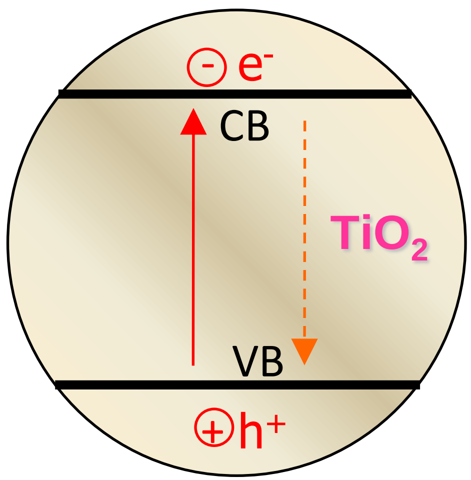
TiO_2 as photocatalyst

"Organic Pollutants" $\xrightarrow[TiO_2]{O_2}$ UV - light **Photodegradation**

Aqueous Media
or
Vapours

TiO_2
Suspension/Thin Films

UV light



REDUCTION

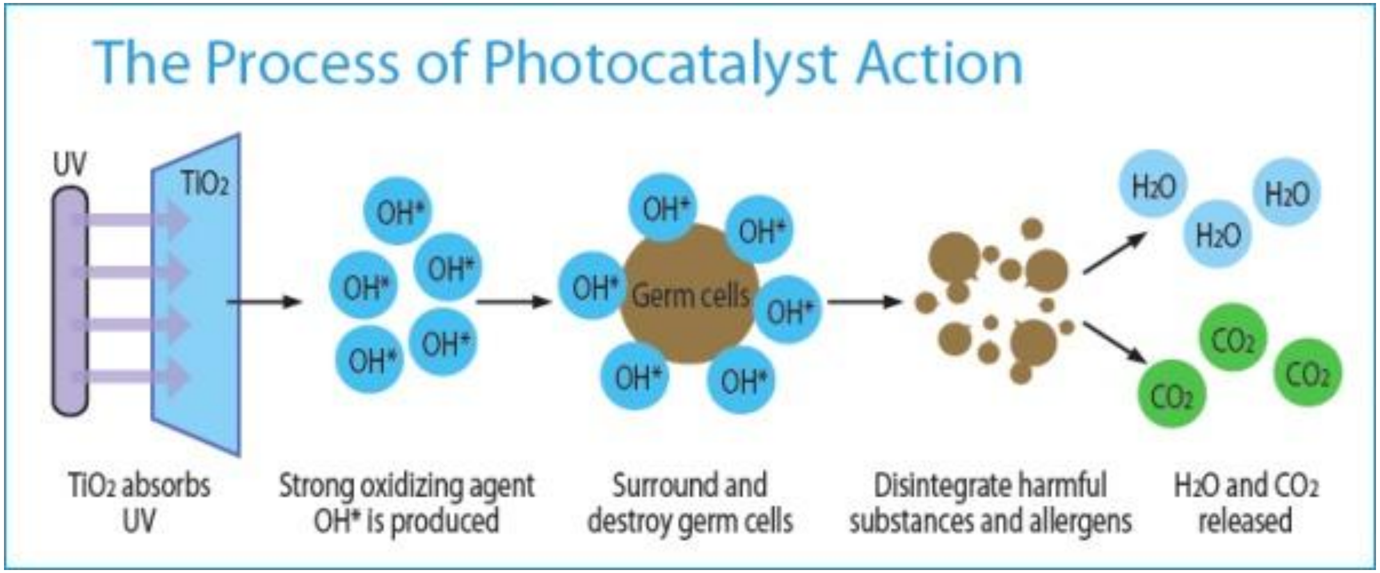
$$A + e^- \longrightarrow A^{-\cdot}$$

$$TiO_2(e^-_{CB}) + O_{2ads} \longrightarrow O_2^{\cdot -}$$

OXIDATION

$$D + h^+ \longrightarrow D^{+\cdot}$$

$$TiO_2(h^+_{VB}) + OH^-_{ads} \longrightarrow TiO_2 + OH^{\cdot}_{ads}$$


The Process of Photocatalyst Action
UV
TiO2
OH*
OH*
OH*
OH*
OH*
OH*
Germ cells
OH*
OH*
OH*
OH*
OH*
H2O
H2O
H2O
CO2
CO2
CO2
TiO2 absorbs UV
Strong oxidizing agent OH* is produced
Surround and destroy germ cells
Disintegrate harmful substances and allergens
H2O and CO2 released

Why TiO_2 ?

- Inert material -at least in absence of light-

- Inexpensive

- Decomposes refractory organic pollutants (dyes, herbicides, pesticides, etc.)

- Reacts at ambient temperature

- Uses a clean energy source---UV light

- Use of O_2 as the only oxidant

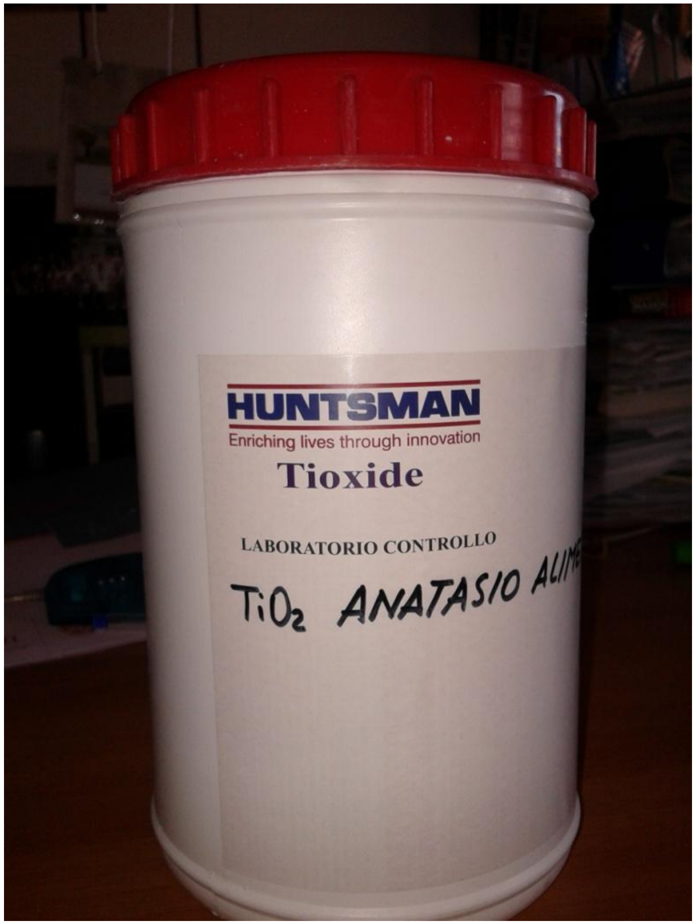
TiO_2 APPLICATIONS

Photocatalytic Cements

“Dives in Misericordia”

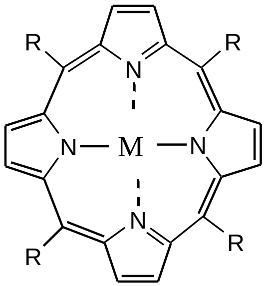
Chiesa delle Vele, Tor Tre Teste, Roma

Edible TiO_2


HUNTSMAN
Enriching lives through innovation
Tioxide
LABORATORIO CONTROLLO
TiO2 ANATASIO

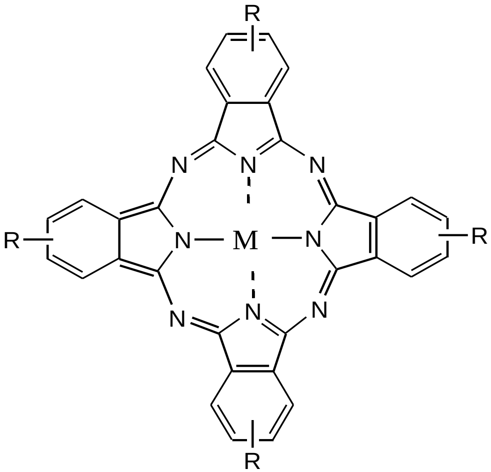

ASPIRIN®
Wirkstoff: Acetylsalicylsäure
BAYER
20 Tabletten N2

Structures of Porphyrins and Phthalocyanines



M-Porphyrins

(M-Pp)



M-Phthalocyanines

(M-Pc)

Macrocyclic systems which contain a large π-electron conjugated system (an aromatic system with 18 π -electrons)

M= Metal ion (or alternatively two hydrogen atoms) in the middle of the structure

R = Various peripheral substituents

MPps & MPcs Multipurpose Materials

They have been applied into new Material areas such as:

☆ Photovoltaics
☆ Electrochromism
☆ Optical Data Storage
☆ Laser Dyes
☆ Liquid Crystals
☆ Chemical Sensors
☆ Photosensitizers for Photodynamic Therapy
☆ Molecular wires, optoelectronic gates
☆ Light-harvesting arrays, integrated antenna-reaction center complexes

Porphyrins ……. Natural materials

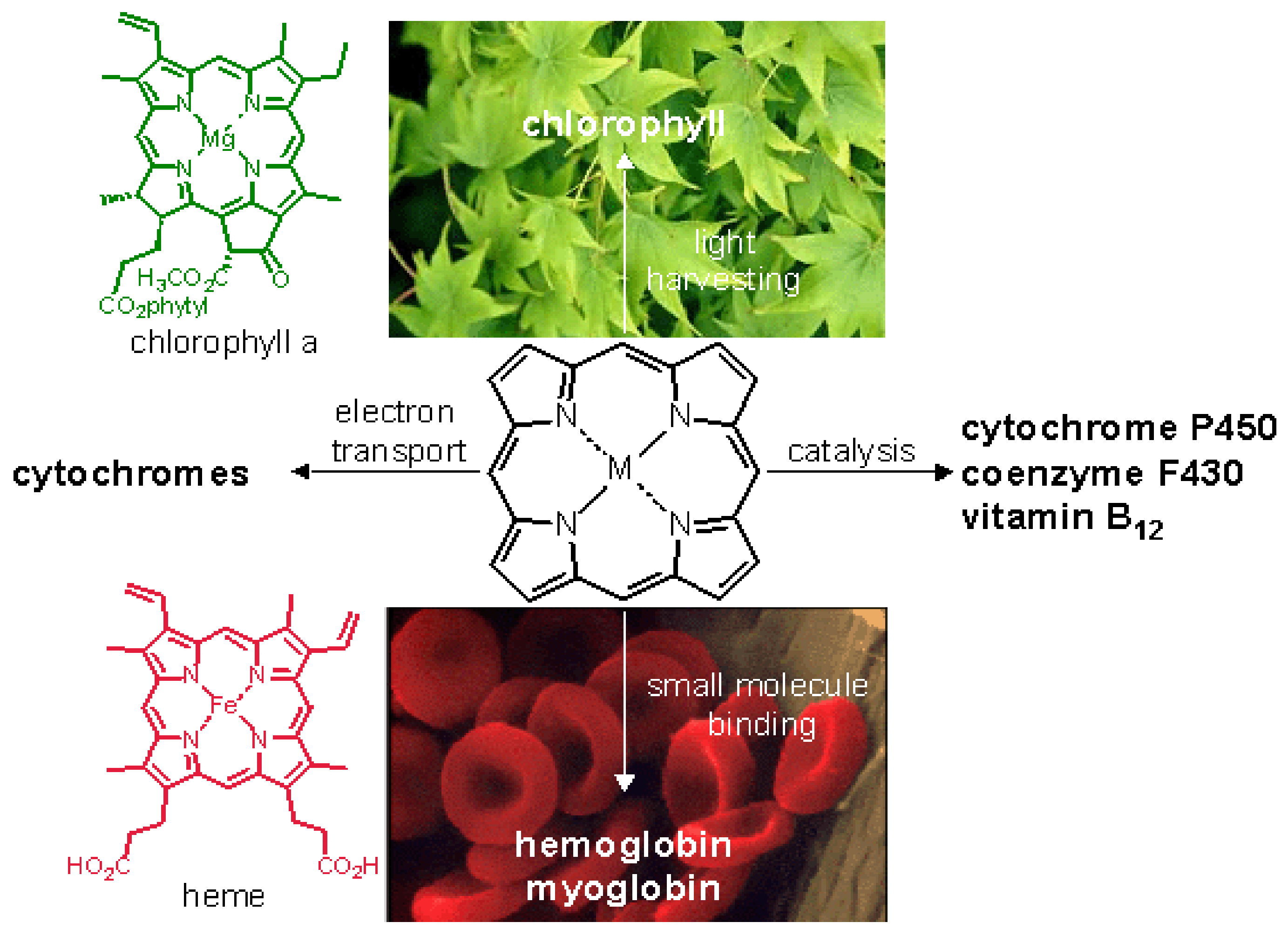
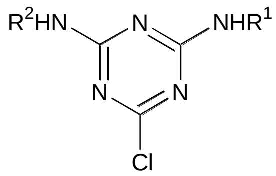


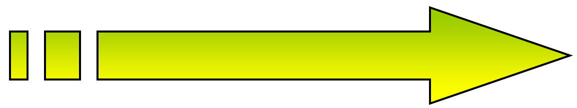
Figure 1. Diverse functions of metalloporphyrins in Nature

Comparative Studies on the Photodegradation of Atrazine



ATRAZINE
Derivatives

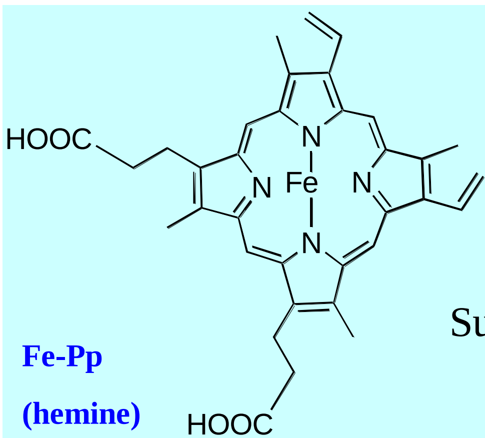
Photocatalytic
Oxidation



"Degradation"

TiO_2

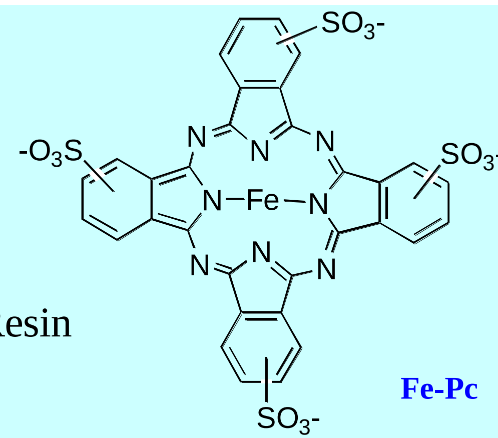
Iron-Porphyrin and Iron-Phthalocyanine



Fe-Pp

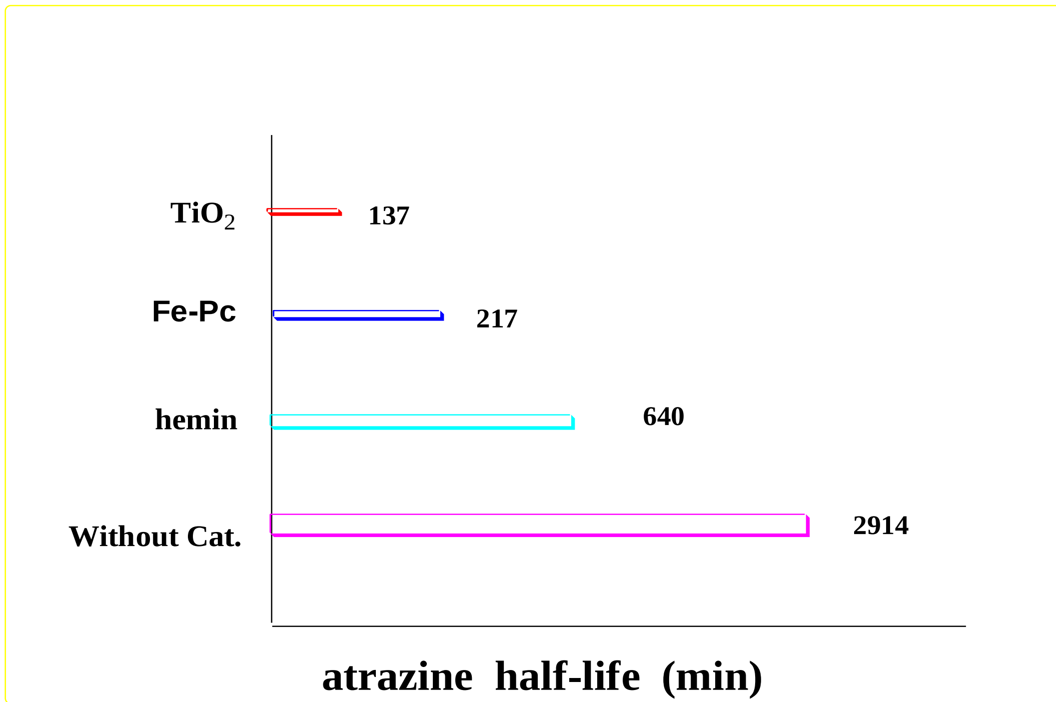
(hemine)

Supported Solid Resin
(Amberlite)



Fe-Pc

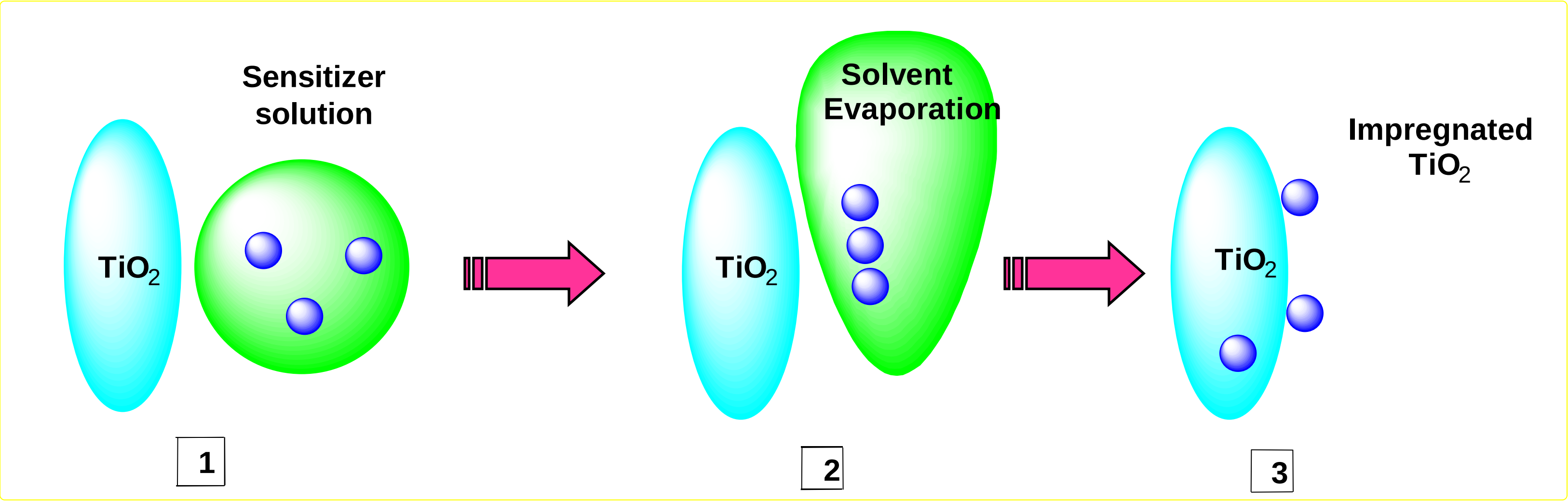
Atrazine degradation with different catalysts



V. Hequet, P. Le Cloirec, G. Gonzalez, B. Meunier, Chemosphere (2000) 379

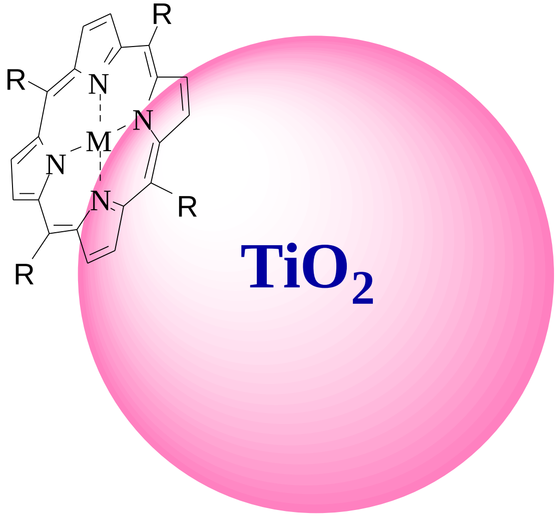
Composite preparation

Impregnation of TiO_2 with MPps or MPcs “Sensitizers”



TiO_2-sensitizer Photocatalytic System

- Sensitizers can be activated by visible light radiation.
- TiO_2 is activated by UV light radiation



Organic pollutants → Degradation

UV-Vis light

“Functional” Porphyrins and Phthalocyanines

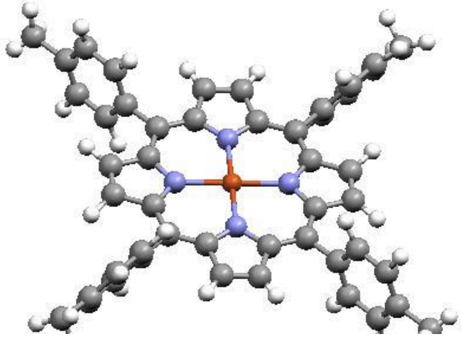
Soluble in Organic Solvents

Insoluble in Water

Thermally and Environmentally Stable

Photoresistant

Organic Sensitizers (itself semiconductors)



Porphyrins

Mele, J. Catal. 2003, 217, 334.
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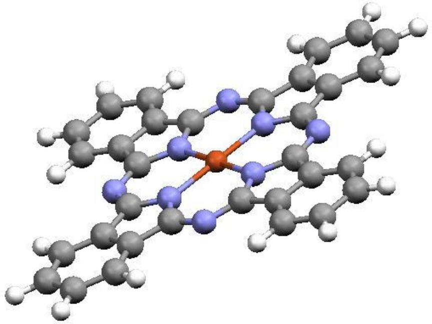
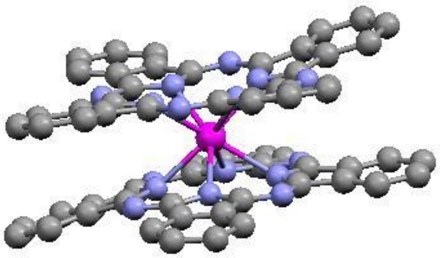
Mele, Li, J. Res. Chem. Intermed. 2007, 33, 433.
Wang, C.; Li, J.; Mele, G.. Appl. Catal. B: Environ. 2007, 76, 218.
Wang, C., Li, J. Mele, G.; Słota, et al Dyes and Pigments 2009, 80, 321.
Vasapollo G., Mele G., Molecules, 16, 5769-5784.
Mele G., Pio I., et al. J. of Catalysts, 2013, 1-7.



Phthalocyanines (mono- or bis-)

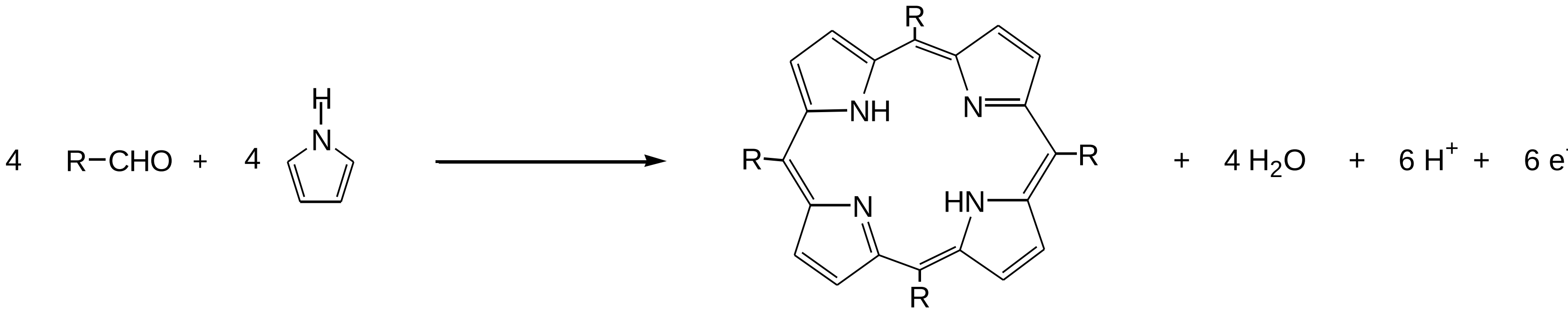


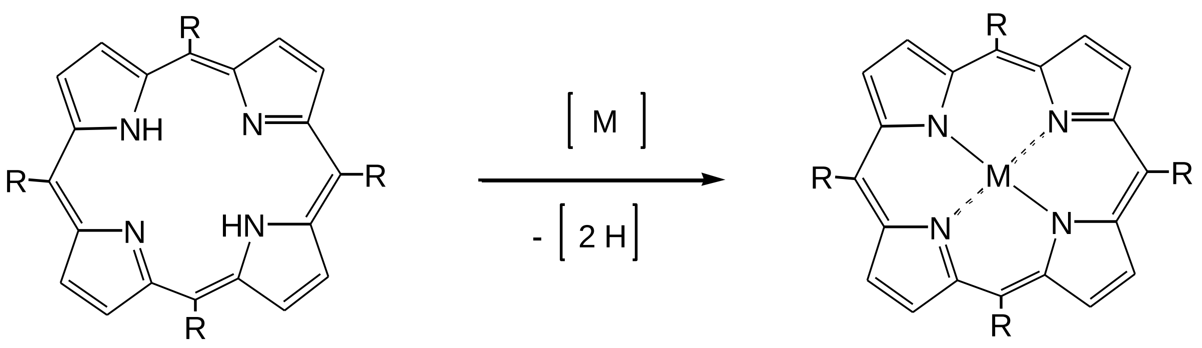
$LnPc_2$

Ln = Ce, Pr, Nd, Sm, Gd, Ho
Z : (58, 59, 60, 62, 64, 67)

Mele, . Appl. Catal. B: Environ. 2002, 38, 309.
Mele, J. Phys. Chem. C, 2007, 111, 6581.
Marcì, Mele, Słota et al. Catalysis Today, 143, 3-4, 30 2009, 203.

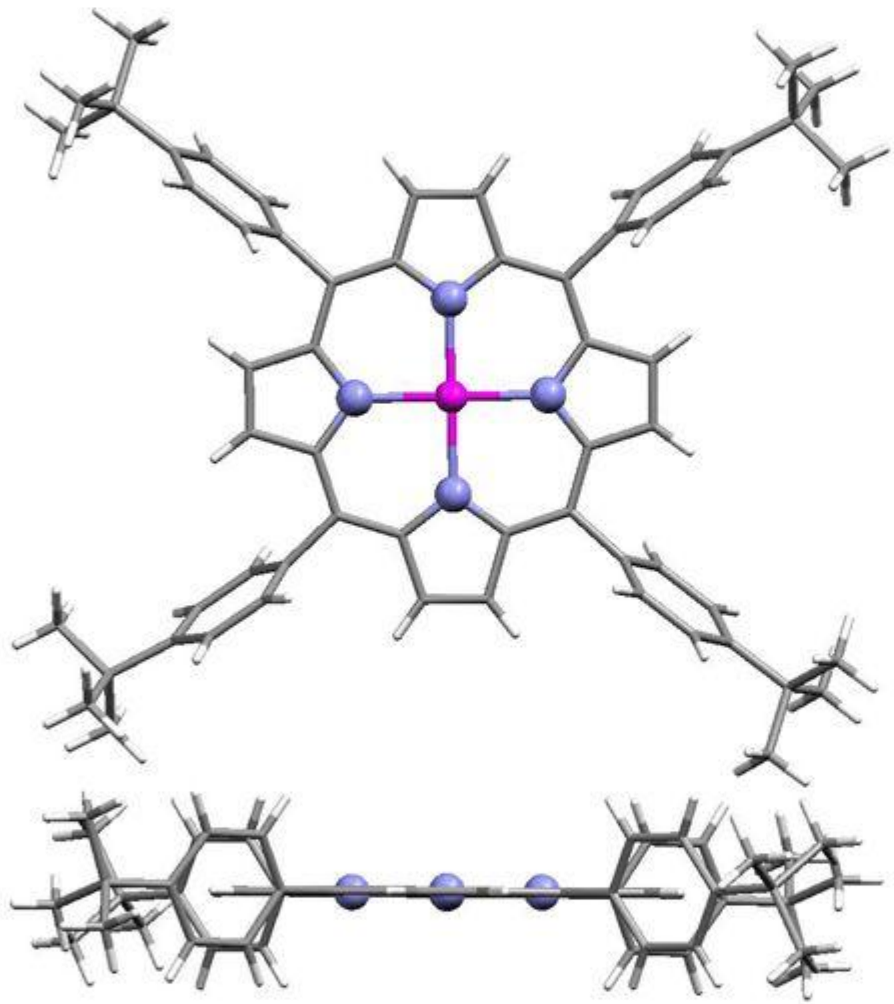
Laboratory Synthesis





M = Cu, Zn, Ni, Co, Fe, Mg, Mn, Si, other

(5,10,15,20-tetra(4-tertbutylphenyl)]porphyrin

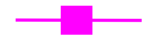
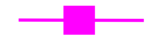
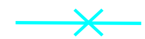


TiO_2

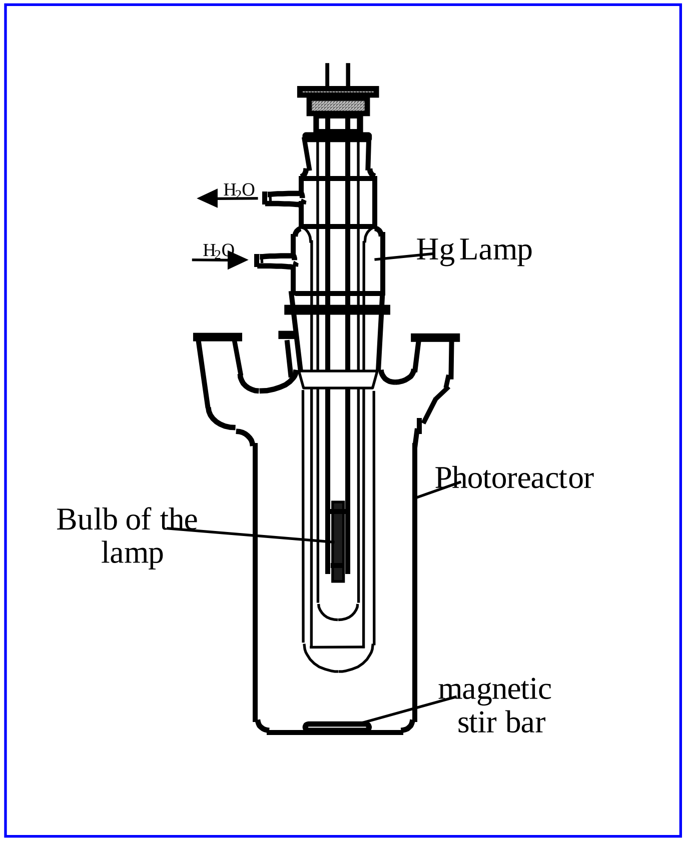
-Tioxide Huntsman-

Pure Anatase

Specific Surface Area
S.S.A. 8 ($m^2 \cdot g^{-1}$)

Catalyst	Symbols [4-NP] vs Irr. Time	Symbols TOC vs Irr. Time
TiO_2 (anatase)		
H_2Pp-TiO_2 (6,56 μmol/g)		
H_2Pp-TiO_2 (11,10 μmol/g)		
CuPp-TiO_2 (3,34 μmol/g)		
CuPp-TiO_2 (5,56 μmol/g)		
CuPp-TiO_2 (6,65 μmol/g)		
CuPp-TiO_2 (8,34 μmol/g)		
CuPp-TiO_2 (11,12 μmol/g)		
CuPp-TiO_2 (13.35 μmol/g)		

Photoreactor



Medium pressure Hg lamp: 125 W

Intensity 13.5 $mWcm^{-2}$

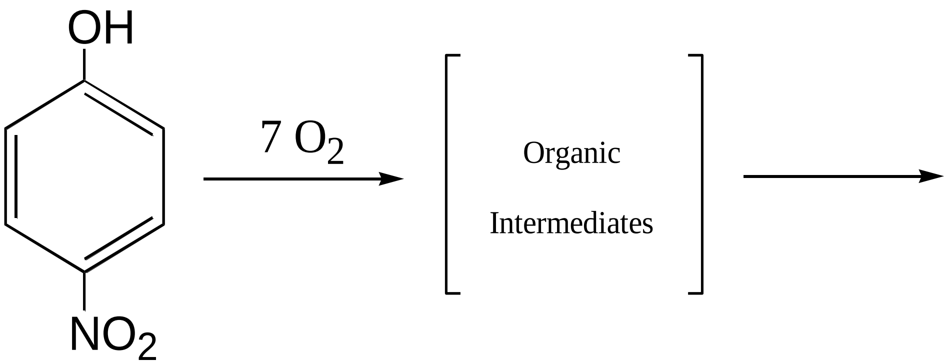
300 nm < λ < 400 nm

Process Conditions

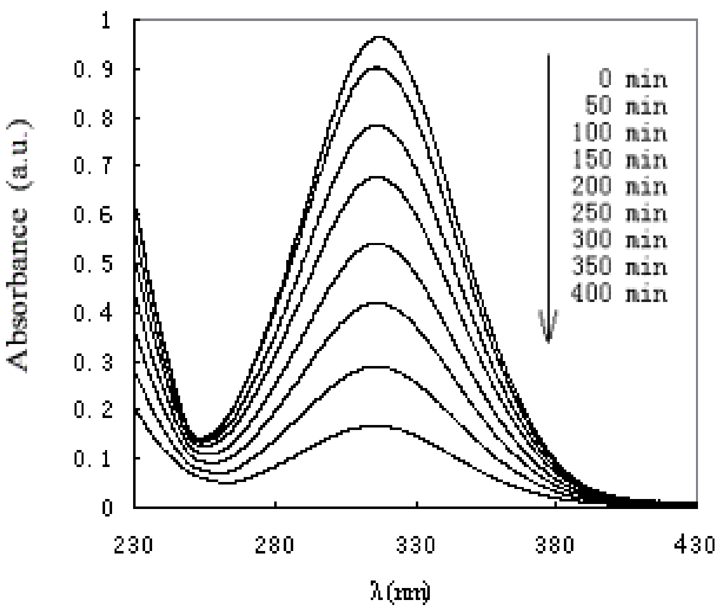
Volume	0.5 L
(4-NP)	20 mg/L
TiO_2 (mod.)	0.8 g/L
pH = 4	(H_2SO_4)
Temperature	300 K

O_2 Bubbled for 30 minutes

“Probe Reaction” - Degradation of 4 Nitrophenol (4-NP)



$$\rightarrow 6\,CO_2 + H^+ + NO_3^- + 2\,H_2O$$

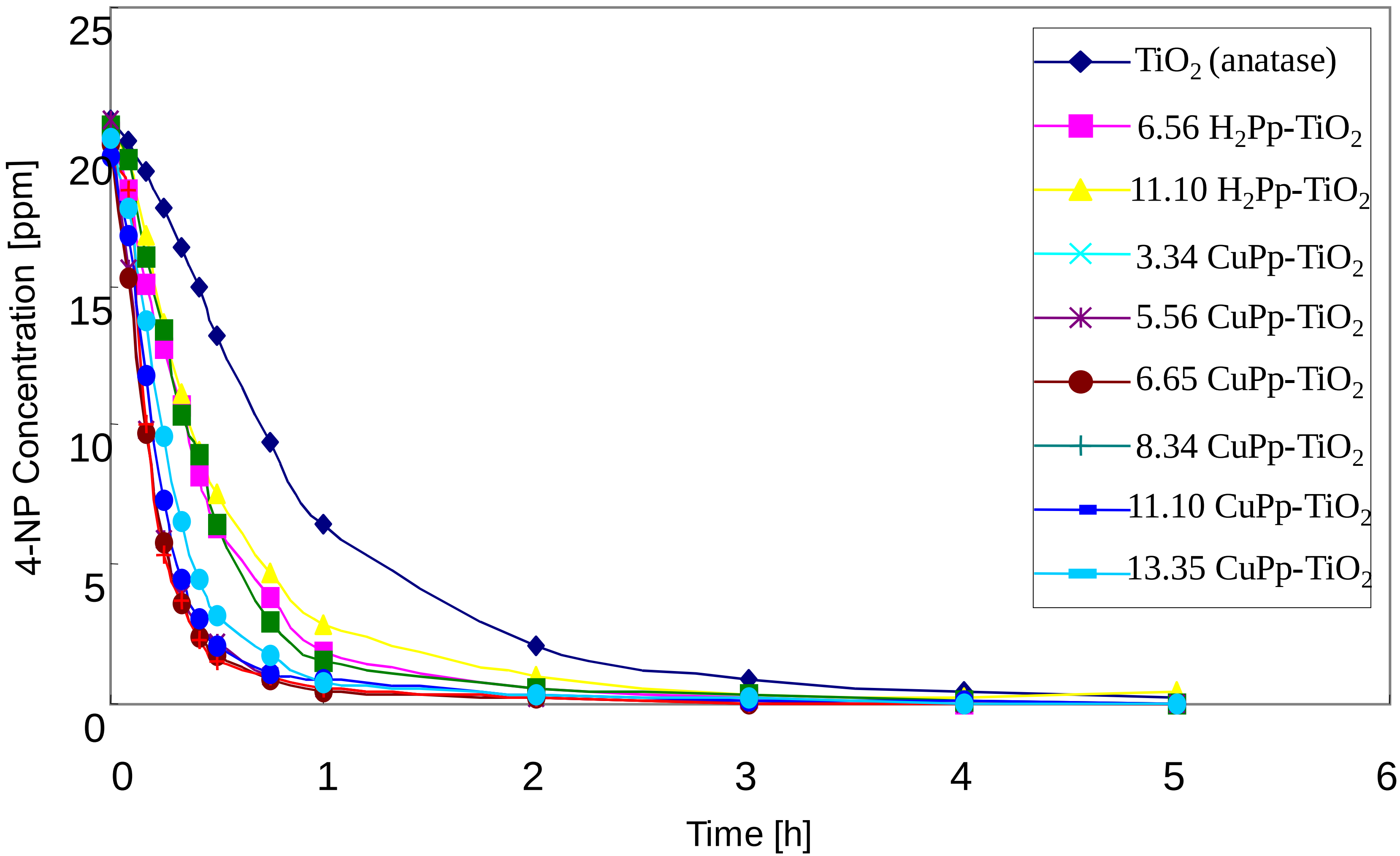


“Mineralization”

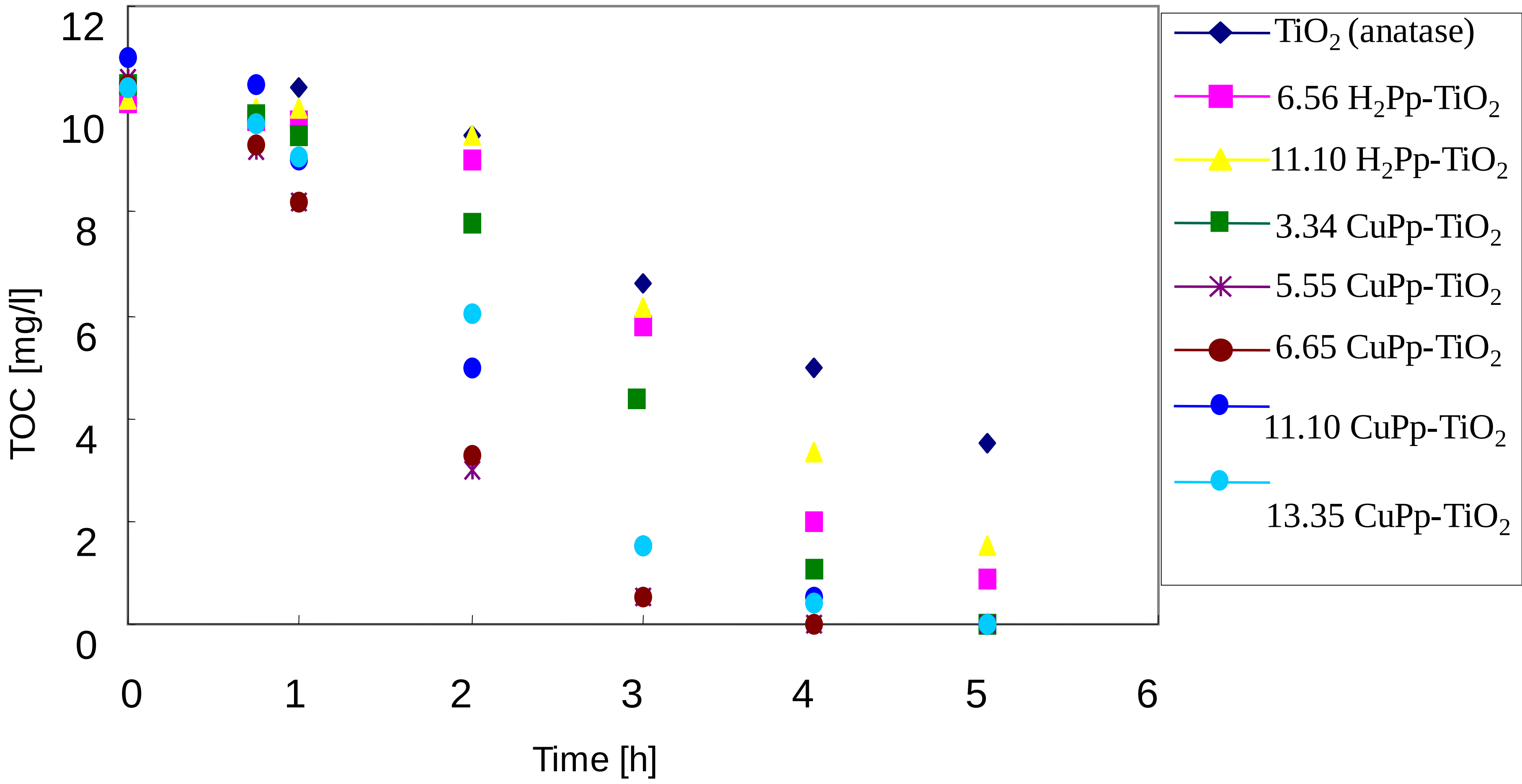
measured by

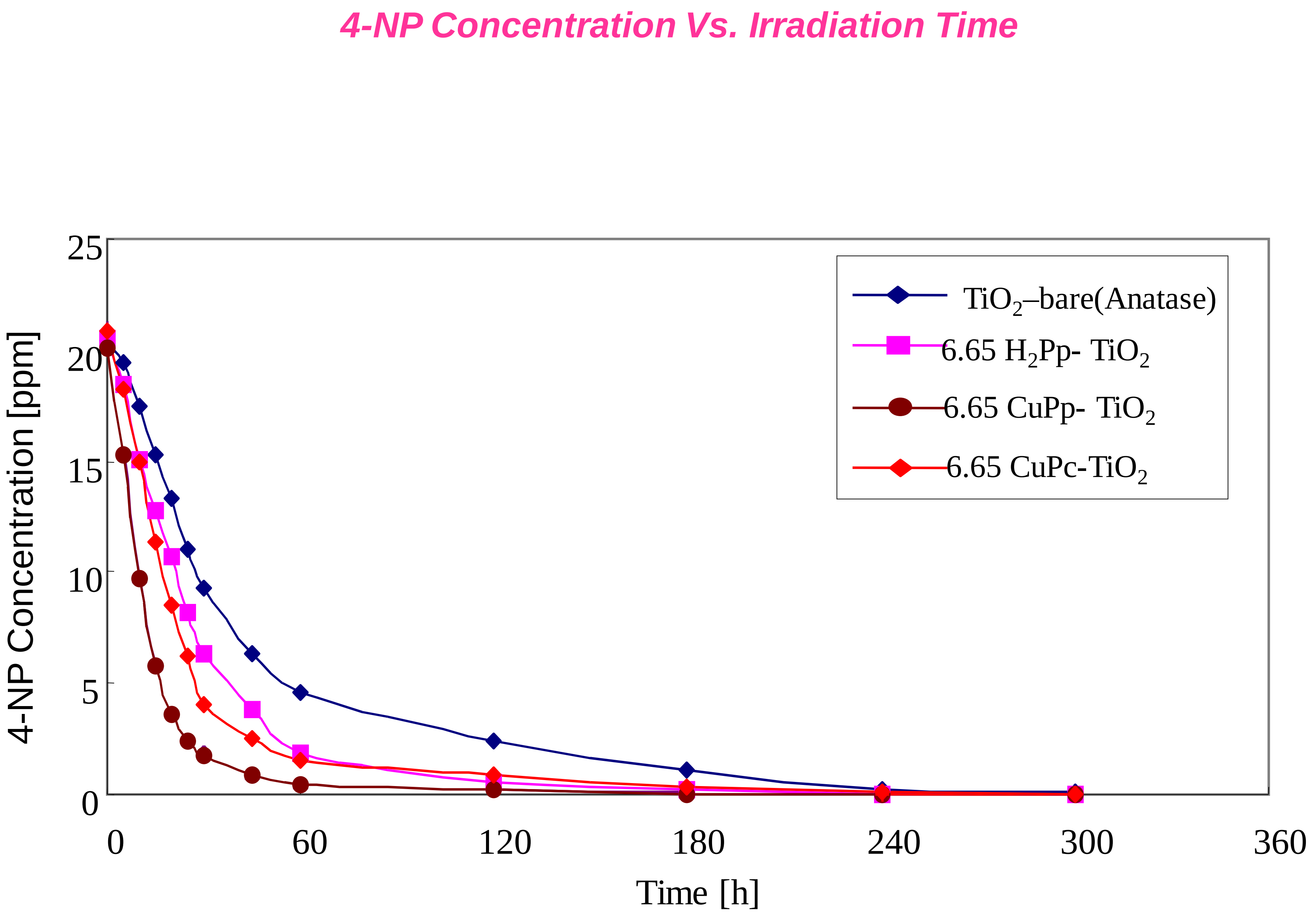
Total Organic Carbon (T.O.C) analysis

4-NP Concentration Vs. Irradiation Time in presence of H2Pp and CuPp



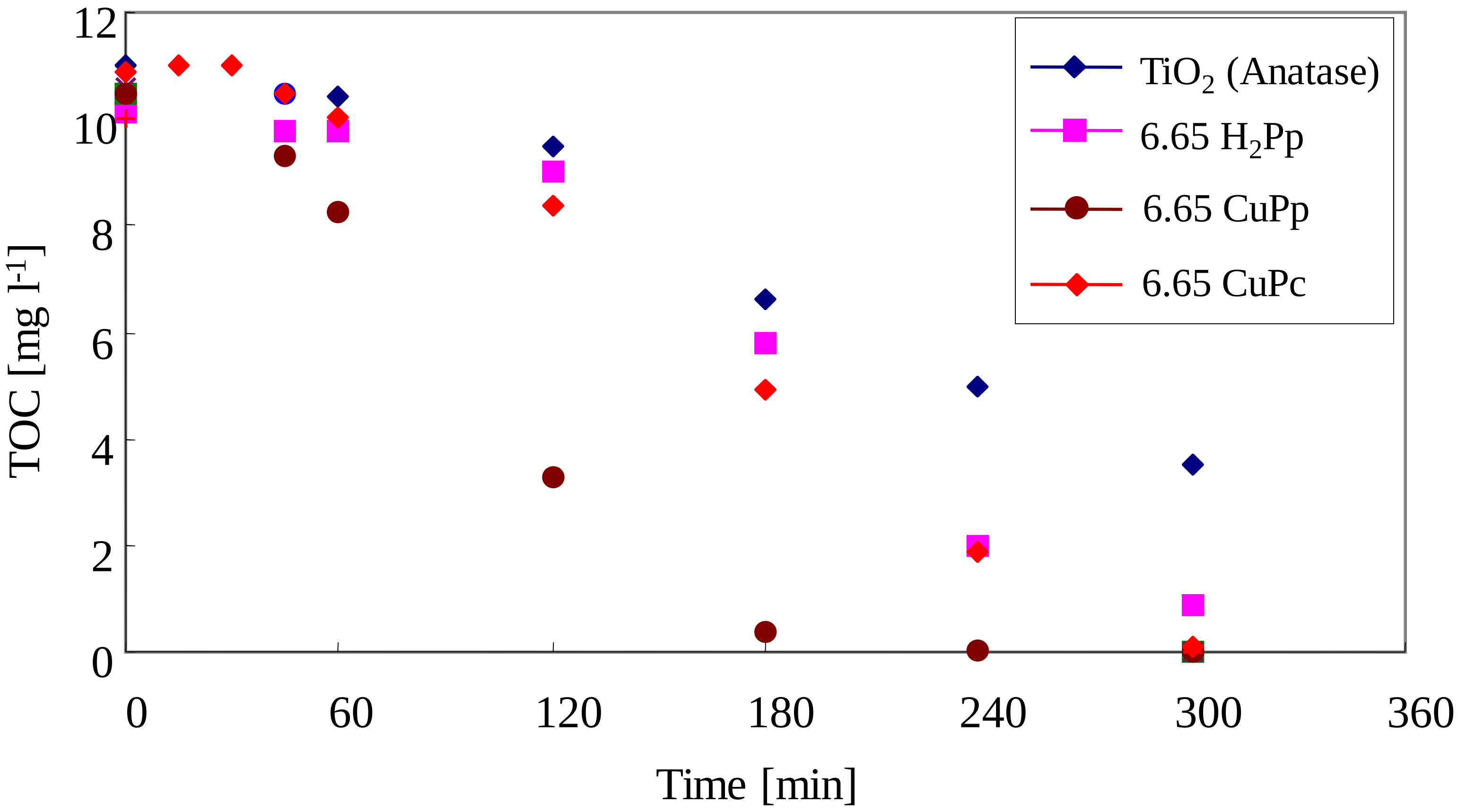
Total Organic Carbon(TOC) Vs. Irradiation Time





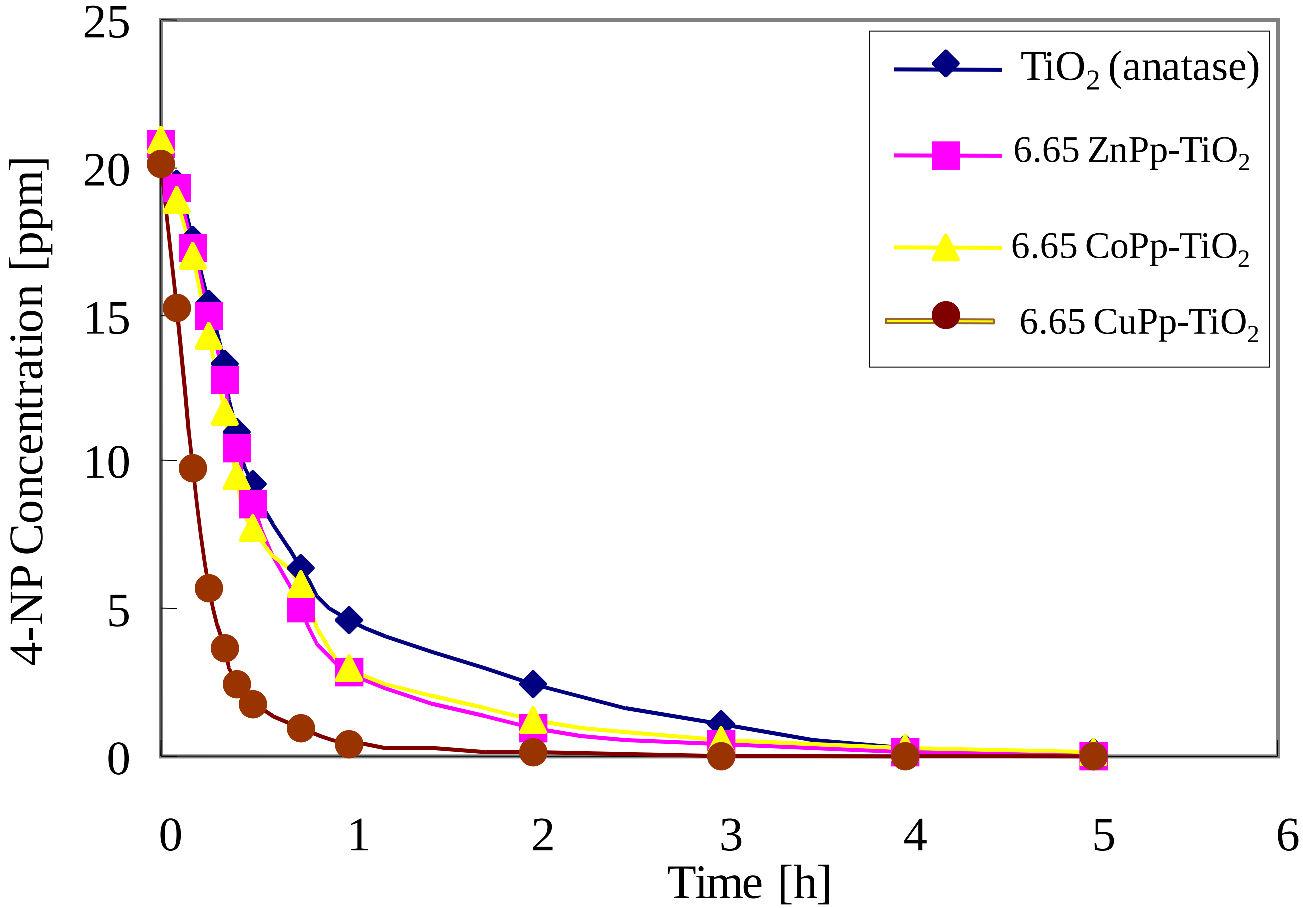
4-NP Concentration Vs. Irradiation Time
4-NP Concentration [ppm]
25
20
15
10
5
0
0
60
120
180
240
300
360
Time [h]
TiO2–bare(Anatase)
6.65 H2Pp- TiO2
6.65 CuPp- TiO2
6.65 CuPc-TiO2

Total Organic Carbon(TOC) Vs. Irradiation Time



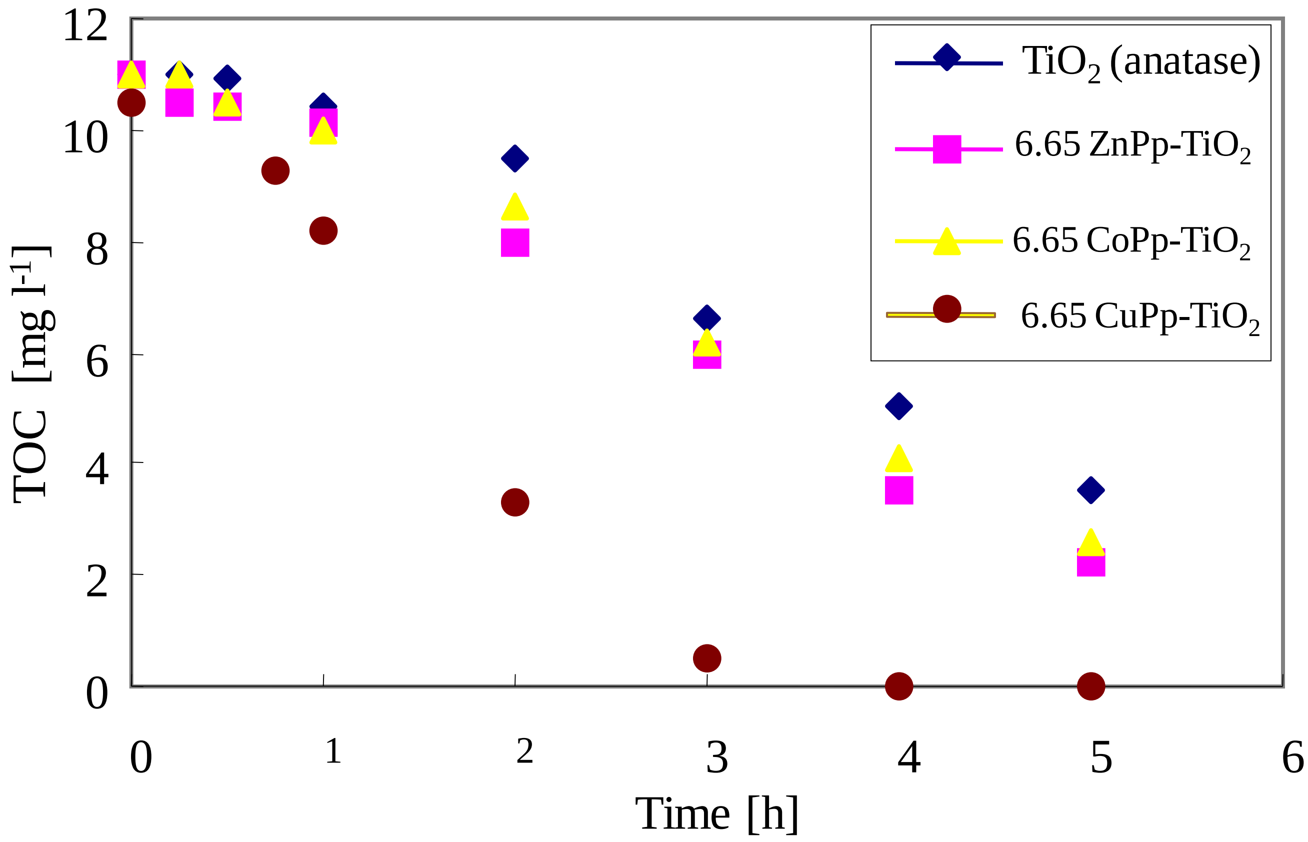
4-NP Concentration Vs. Irradiation Time

in Presence of Zn-Pp Co-Pp and Cu-Pp



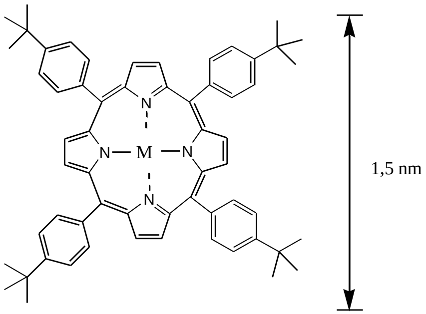
CuPp- TiO_2 > ZnPp-TiO_2 = CoPp- TiO_2 > TiO_2

Total Organic Carbon (TOC) *vs* Irradiation Time



Samples	B.E.T. Specific Surface Areas S.S.A. ($m^2 \cdot g^{-1}$)	Total Areas[a] m^2	$r_0 \cdot 10^{10}$ ($mol \cdot l^{-1} \cdot s^{-1}$)	$r'_0 \cdot 10^{10}$ ($mol \cdot l^{-1} \cdot s^{-1} \cdot m^{-2}$)	η (%) quantum efficiencies
TiO_2(A)	8		467	146	0.7
6.65-TiO_2(A)-H_2Pp	8	9	606	189	0.9
11.10-TiO_2(A)-H_2Pp	8	15	569	178	0.9
3.30-TiO_2(A)-CuPp	8	4.5	595	190	0.9
5.55-TiO_2(A)-CuPp	**8**	**7.5**	**1225**	**383**	**1.9**
6.65-TiO_2(A)-CuPp	**8**	**9**	**1162**	**363**	**1.8**
8.35-TiO_2(A)-CuPp	8	11	1087	352	1.7
11.10-TiO_2(A)-CuPp	8	15	950	315	1.5
13.30-TiO_2(A)-CuPp	8	18	854	271	1.3
6.65-TiO_2(A)-CuPc	8	9	755	236	1.2
6.65-TiO_2(A)-H_2Pc	8	9	454	142	0.7
11.10-TiO_2(A)-H_2Pc	8	15	359	122	0.5

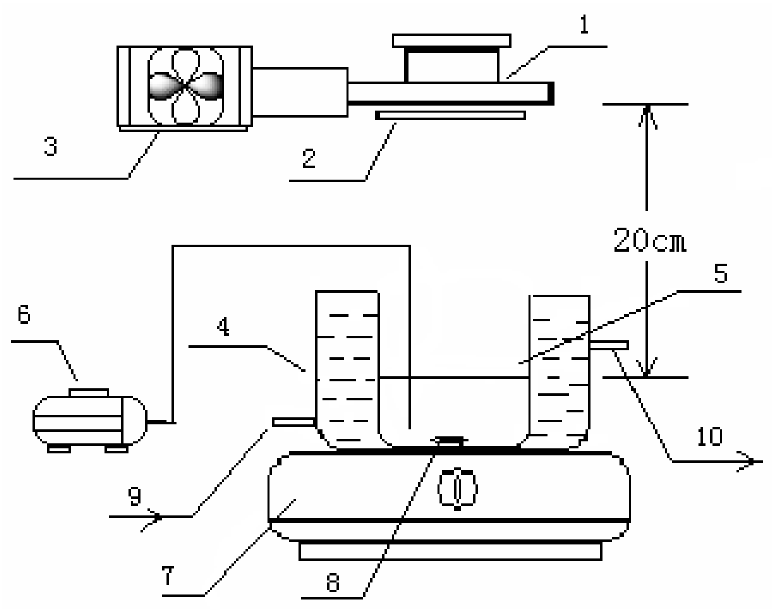
(*a*) The surface area for a single porphyrin molecule was approximate to 2.25 nm^2/molecule. The porphyrins were supposed flat onto the TiO_2 surface.



Mele G. et al.,

J. Catal. 2003, 217, 334.

Photocatalytic experimental set-up



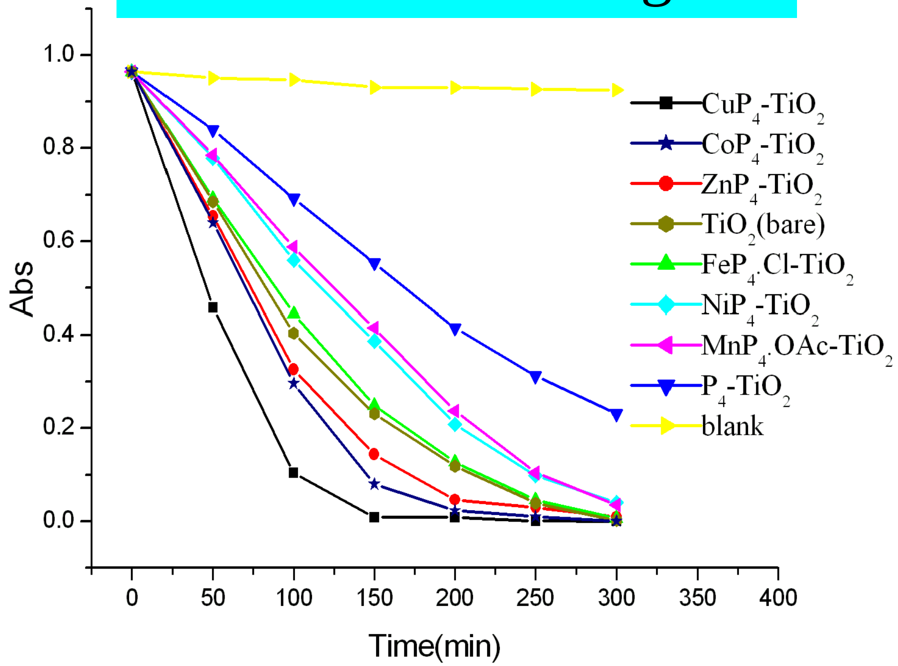
1. Xenon lamp
2. filter
3. cool-fanner
4. constant temperature water jacket
5. reaction beaker
6. air pump
7. magnetic stirrer
8. magneton
9,10. inlet and outlet of water

500 W, 24 V xenon lamp
(CHF-XM35-500W, Beijing Trusttech Co., Ltd., China) providing UV-vis light.

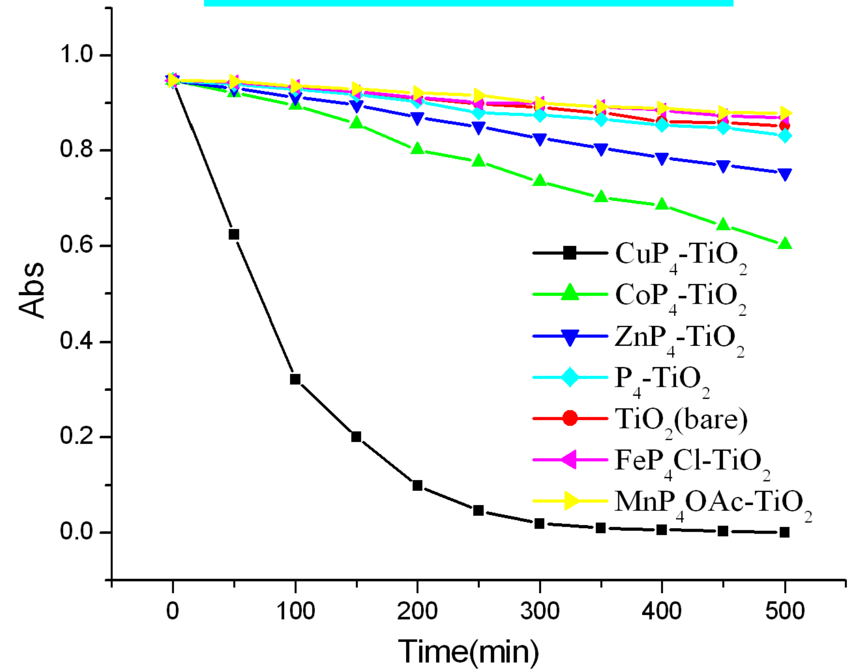
Distance 110 cm
light intensity was 4.061 mW/cm^2 (New Port Dual-Channel Power Meter, model 2832-C, Irvine, CA).

Photocatalytic activity for 4-NP degradation

Under UV-visible light

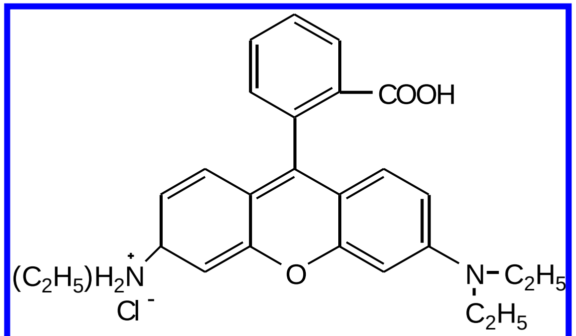


Under visible light

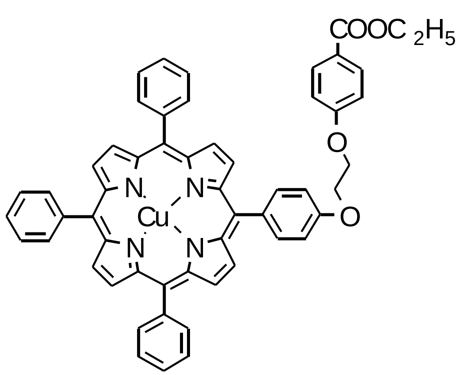


- CuP_4-TiO_2, CoP_4-TiO_2 and ZnP_4-TiO_2 have higher photocatalytic activity than bare TiO_2;
- CuP_4-TiO_2 is the most effective photocatalyst under UV-visible or visible light.

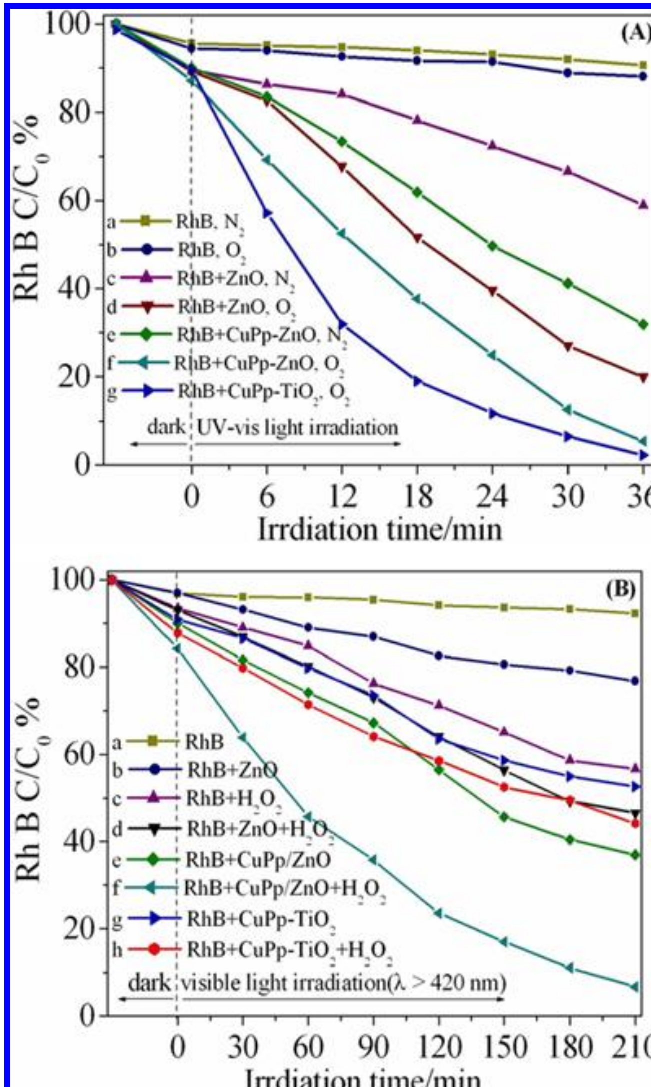
Photodegradation of Rhodamine B



Rhodamine B



CuPp porphyrin



Fe-TiO_2 catalyst

TiO_2 Anatase Powder

BET specific surface area = 8 m^2/g

(TIOXIDE Huntsman)

PHOTO-FENTON PROCESS

UV-vis-Fe/TiO_2-H_2O_2

4-nitrophenol degradation

WET IMPREGNATION

$Fe(NO_3)_3 \cdot 9H_2O$

1wt%Fe, 3wt%Fe, 5wt%Fe, 8wt%Fe

CALCINATION

5 h at 350°C

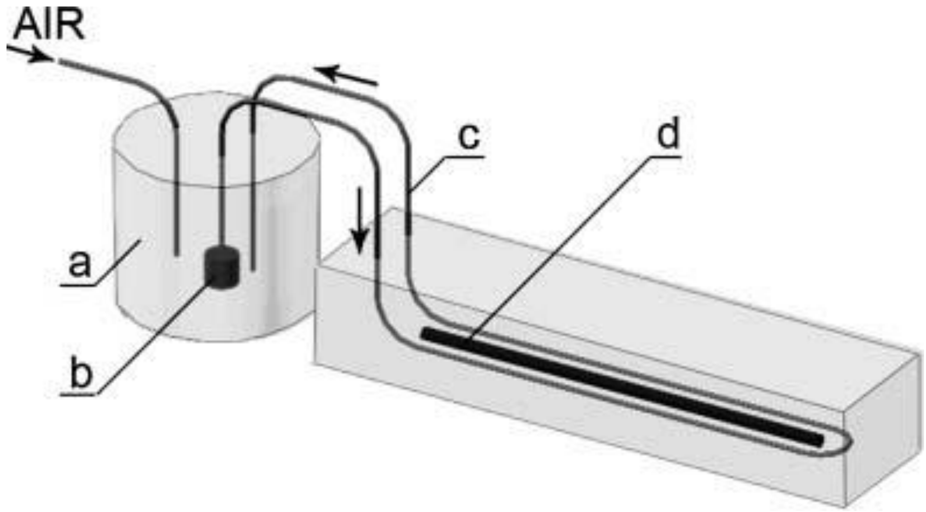
INVESTIGATION PARAMETERS

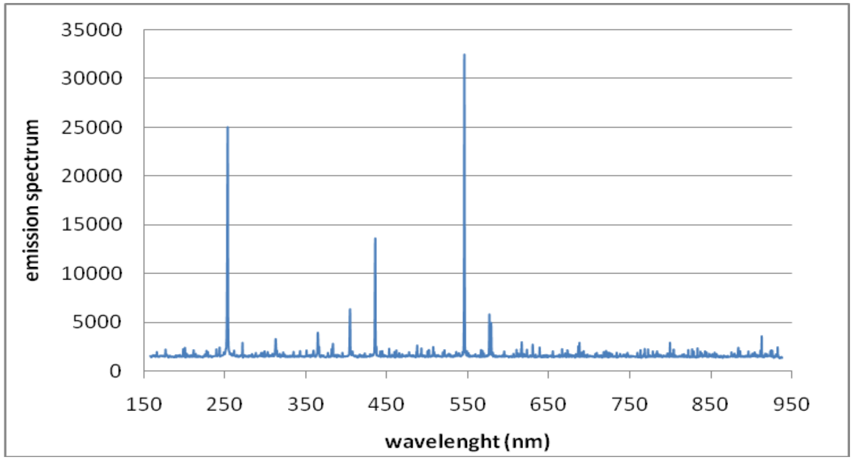
- Fe loading amount
- Amount of Fe-TiO_2 catalyst
- H_2O_2 concentration
- Initial pH of solution

PHOTOCATALYTIC EXPERIMENTS

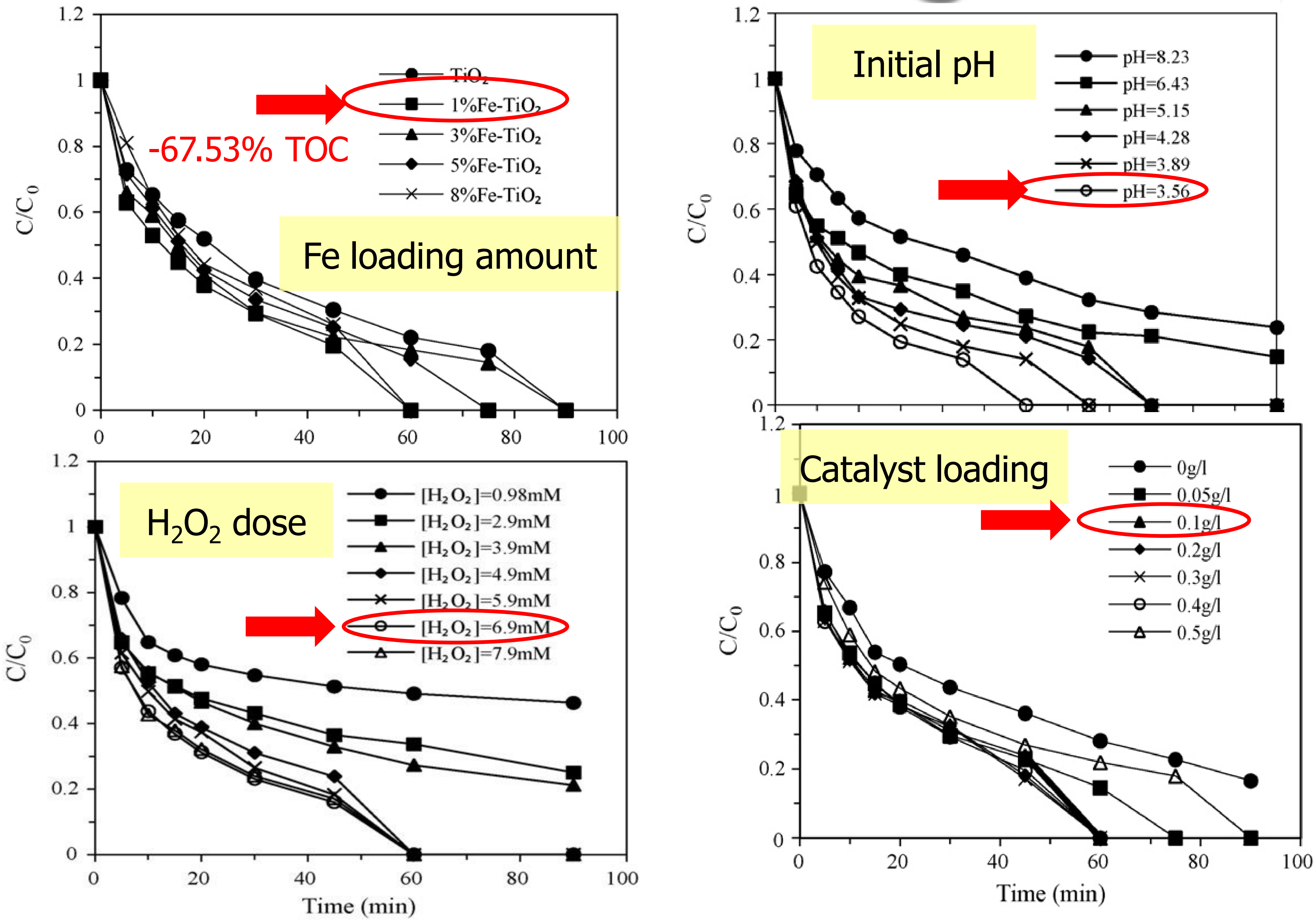
UNIVERSITÀ DEL SALENTO

- ECO 12 H Photoreator (NOVUS-Brindisi)
- UV Lamp
- Radiant flux=100 μW/cm² (290-390 nm)
- V suspension= 2L





Germicidal lamp
(SANKYO DENKY, P=16 W, λ=265 nm)



Fe loading amount
-67.53% TOC
TiO$_2$
1%Fe-TiO$_2$
3%Fe-TiO$_2$
5%Fe-TiO$_2$
8%Fe-TiO$_2$
Initial pH
pH=8.23
pH=6.43
pH=5.15
pH=4.28
pH=3.89
pH=3.56
H$_2$O$_2$ dose
[H$_2$O$_2$]=0.98mM
[H$_2$O$_2$]=2.9mM
[H$_2$O$_2$]=3.9mM
[H$_2$O$_2$]=4.9mM
[H$_2$O$_2$]=5.9mM
[H$_2$O$_2$]=6.9mM
[H$_2$O$_2$]=7.9mM
Catalyst loading
0g/l
0.05g/l
0.1g/l
0.2g/l
0.3g/l
0.4g/l
0.5g/l
C/C$_0$
Time (min)

EXPERIMENTAL

Recycling of catalysts

Recovering by filtration

Washing with UP water

Drying at 110°C overnight

Re-using in the same conditions

Cycle	TOC (%)
1	67.53
2	64.17
3	62.32
4	66.26

Fe-leaching evaluation

ICP Spectrometer

(THERMO SCIENTIFIC iCAP 6000 SERIES)

$[Fe^{3+}]_{solution} = 1 \div 8$ ppb

$[Fe^{3+}]_{TiO_2\ surface} = 1 \div 40$ ppm

NEGLIGIBLE LEACHING

ABSENCE OF SIGNIFICANT DEACTIVATION

Journal of Hazardous Materials 176 (2010) 569 B. Zhao, G. Mele, I. Pio, J. Li, L. Palmisano, G. Vasapollo

Scarico in fognatura

Trattamento primario:
Grigliatura
Dissabbiatura
Disoleazione

Trattamento secondario: vasca di trattamento per fosforo e azoto

Trattamento secondario: vasca di trattamento biologico

Trattamento secondario: Sedimentazione e disinfezione

Scarico in corpo idrico recettore (mare)

Ingresso all'affinamento

Prelievo campione A di "INGRESSO"

Dosaggio in-linea e miscelazione simultanea di sostanze coagulanti, adsorbenti e disinfettanti

Flocculazione, contatto prolungato e sedimentazione avanzata in vasca

Disinfezione fisica UV con modalità in-linea e in ricircolo

Prelievo campione B di "USCITA"

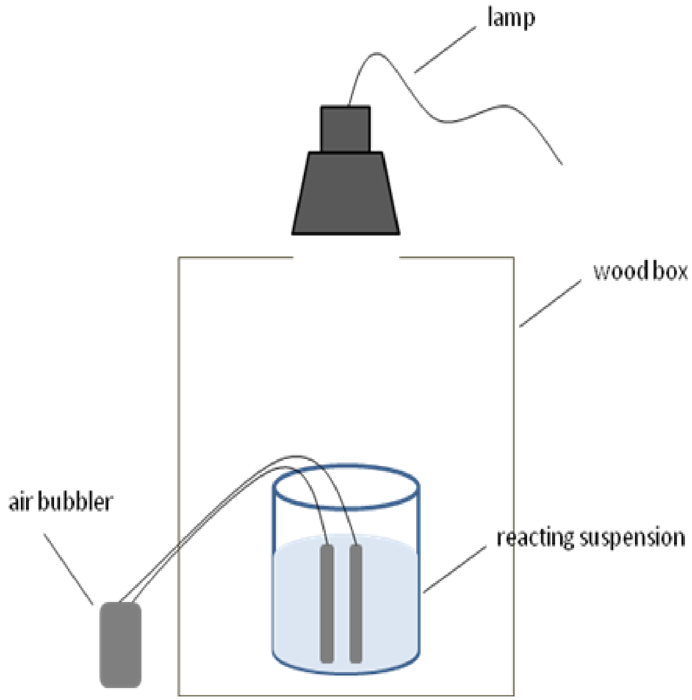
DISTRIBUZIONE E RIUTILIZZO

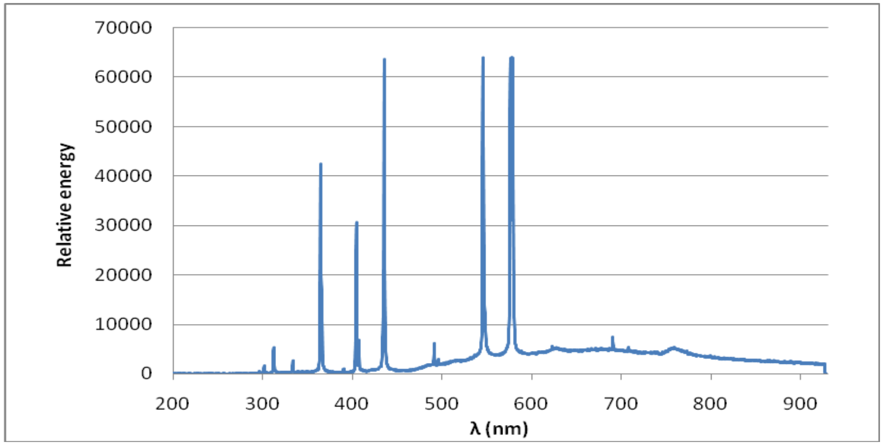
CARATTERIZZAZIONE ACQUE REFLUE (FASANO)

ANION	SAMPLE A (IN) [ppm]	SAMPLE B (OUT) [ppm]
F^-	0.52	0.101
Cl^-	456.20	589.050
Br^-	0.76	0.928
NO_3^-	68.16	66.982
PO_4^{3-}	19.62	9.998
SO_4^{2-}	120.91	98.250

CATION	SAMPLE A (IN) [ppm]	SAMPLE B (OUT) [ppm]
Na^+	229.46	228.31
K^+	25.52	27.03
Mg^{++}	28.81	28.60
Ca^{++}	61.06	58.35

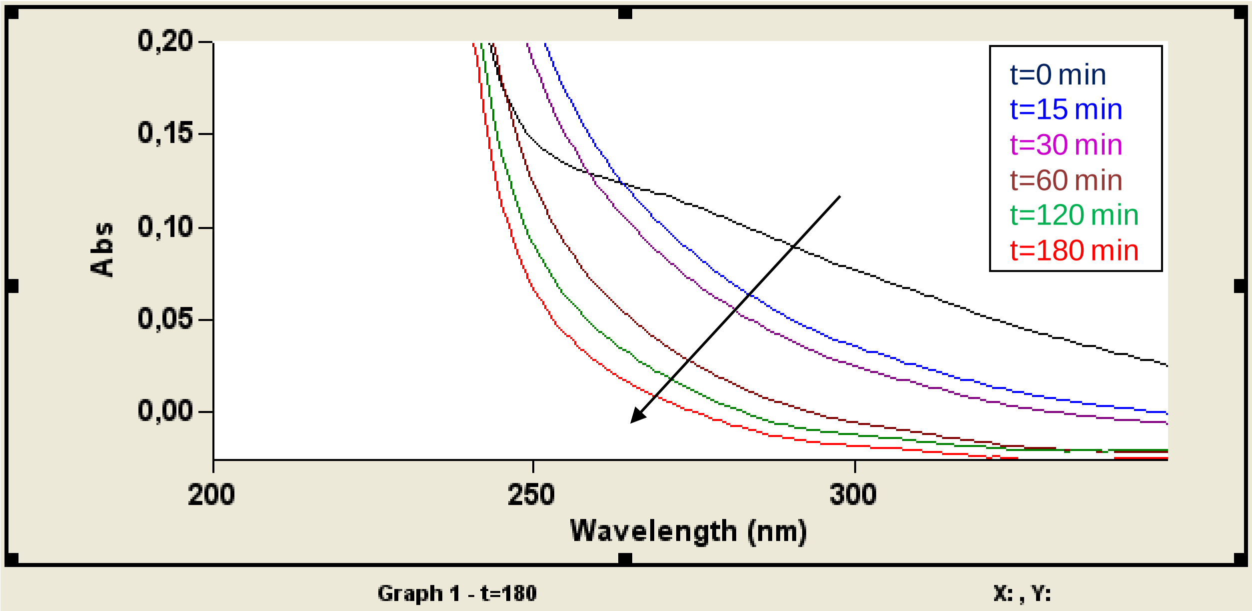
SAMPLE	**CONDUCTIVITY (μS)**
A (ingresso)	4020
B (uscita)	1550





Emission spectrum of SANOLUX HRC UV-vis lamp

Lampada SANOLUX HRC 300W
Amount Cat. =0.2 g/L,1% Fe-TiO_2
[H_2O_2]=4.9 mM
V=300 mL



UV-vis Spectra (range 200-350 nm)
Sample (A) from AquaSoil s.r.l. plant

Sample A	IC (mg/l)	TC (mg/l)	TOC (mg/l)
Wastewater 0 min irr	46,20	76,63	30,43
Wastewater 180 min. irr.	39,17	52,82	13,65

Northwest University

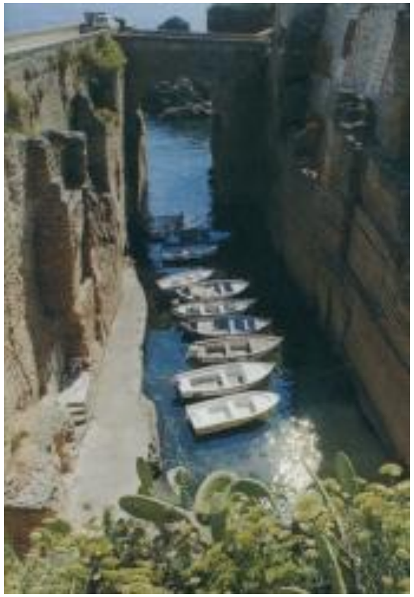
Xi’an - China

UNIWERSYTET OPOLSKI

University of Opole

UNIVERSIDADE FEDERAL
DO CEARÁ
DEPARTAMENTO DE
QUÍMICA ORGÂNICA E INORGÂNICA

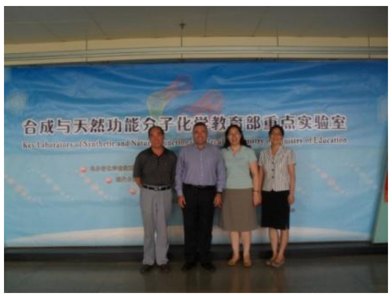
Selma Mazzetto-UFC (Brazil)



Same view of Lecce area

UNIVERSIDADE FEDERAL
DO CEARÁ

University of Palermo
Leonardo Palmisano
Giuseppe Marcì
Elisa Garcìa Lòpez



Ελληνική Δημοκρατία

Ευρωπαϊκή Επιτροπή

Ιταλική Δημοκρατία

INTERREG III A ΕΛΛΑΔΑ-ΙΤΑΛΙΑ
ΠΡΟΓΡΑΜΜΑΤΙΚΗ ΠΕΡΙΟΔΟΣ 2000-2006

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Department of Engineering for Innovation

UNIVERSITY OF SALENTO, ITALY

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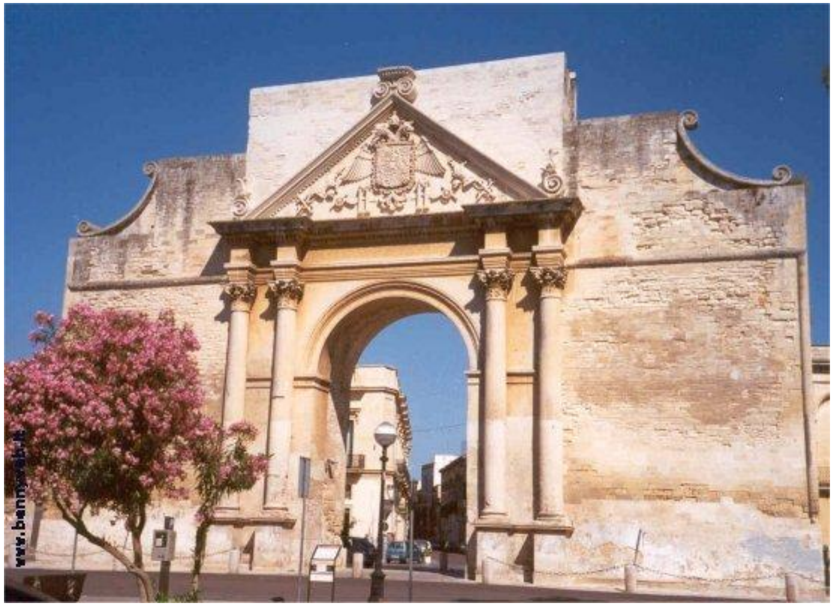
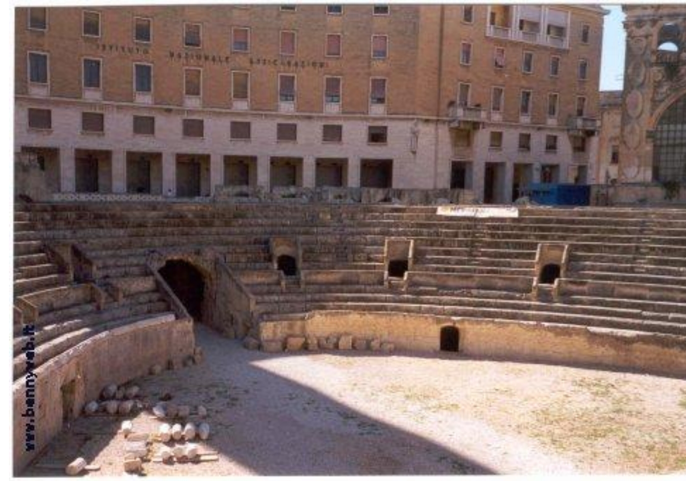
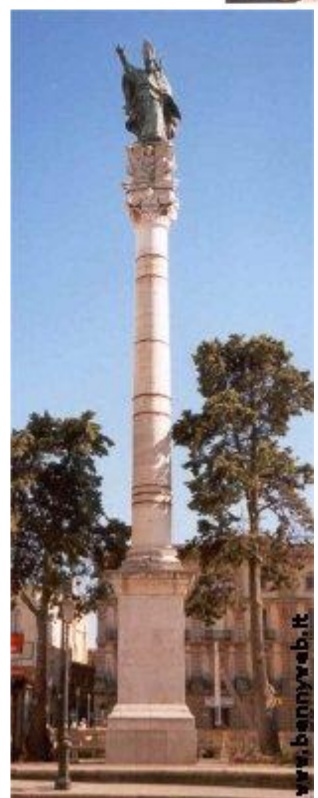


PORTA NAPOLI



ANFITEATRO ROMANO

DUOMO

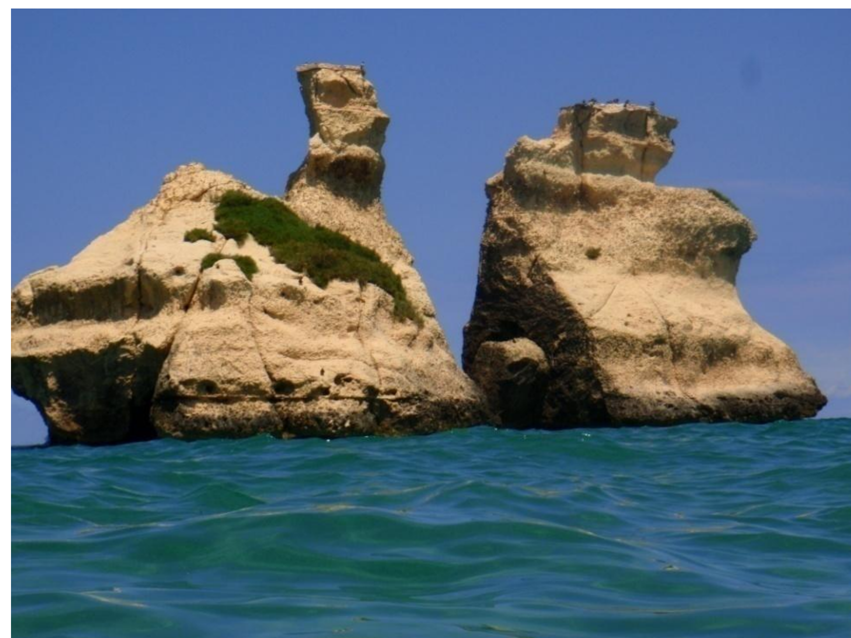


STATUA DI S. ORONZO

BASILICA DI S. CROCE

Some monuments in Lecce City



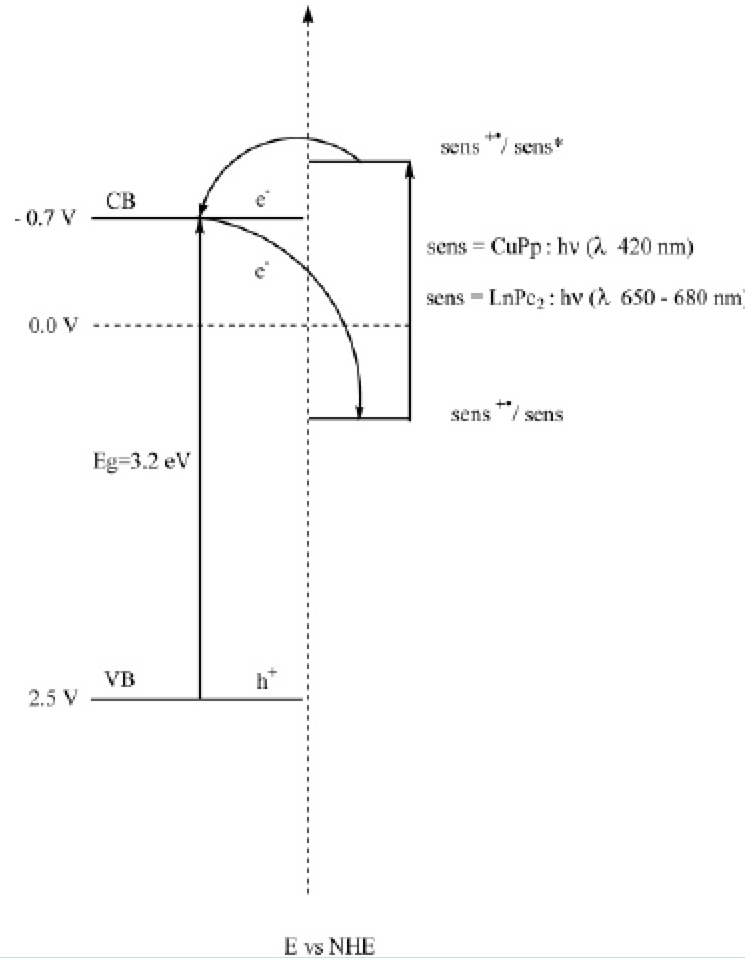
Trento
Aosta
Milano
Verona
Trieste
Torino
Venezia
Parma
Bologna
Genova
SAN MARINO
Firenze
Ancona
MAR ADRIATICO
ITALIA
L'Aquila
CITTÀ DEL VATICANO
Roma
Bari
Napoli
LECCE
MAR TIRRENO
SARDEGNA
MAR IONIO
Catanzaro
Cagliari
Palermo
Messina
SICILIA
Catania
MAR MEDITERRANEO

“Mechanicistic Details”

Role of TiO_2

$$TiO_2[Cu(II)Sens] \xrightarrow{h\nu\ (<394\ nm)} TiO_2[Cu(II)Sens]\ (e^-_{CB} + h^+_{VB})$$

SCHEME 1: Conduction Band (CB) and Valence Band (VB) Energy Levels of Anatase TiO_2 at Neutral pH and Generalities of Redox Potentials of the Various Sensitizers Considered in this Study



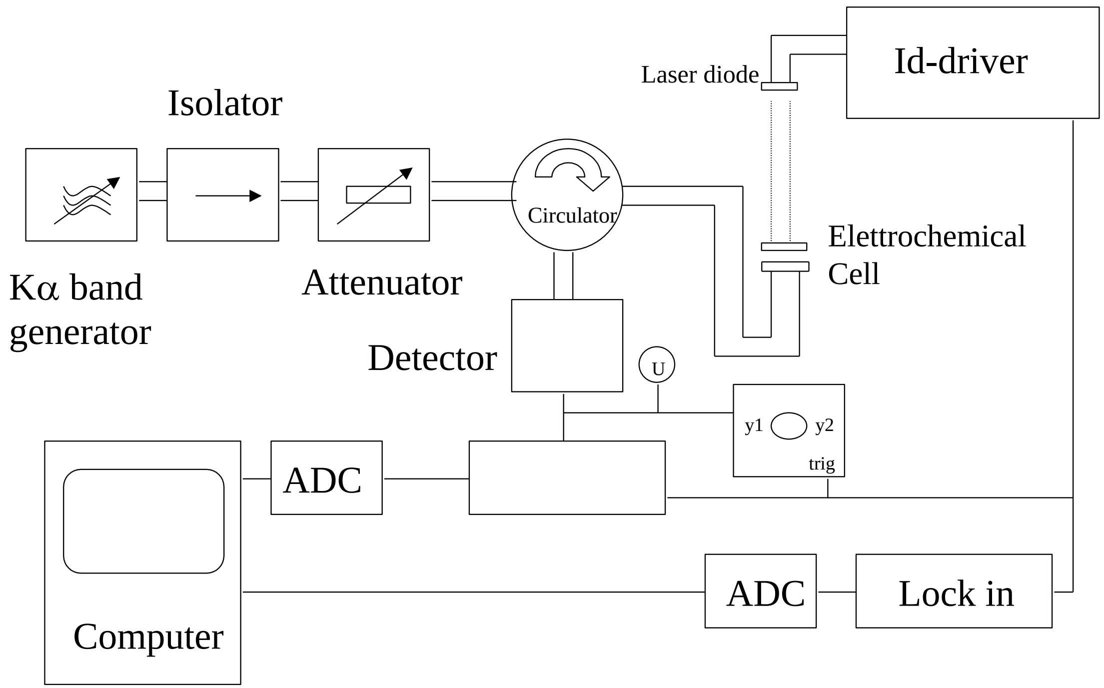


Figure 1. Set-up for the time-resolved microwave conductivity (TRMC) experiments.

DAAD (Deutscher Akademischer Austausch Dienst) for the supply of a fellowship to carry out the measurements on lifetimes of photo-induced excess charge carriers in Hahn Meitner Institut, Berlin (German), and Prof. H. Tributsch

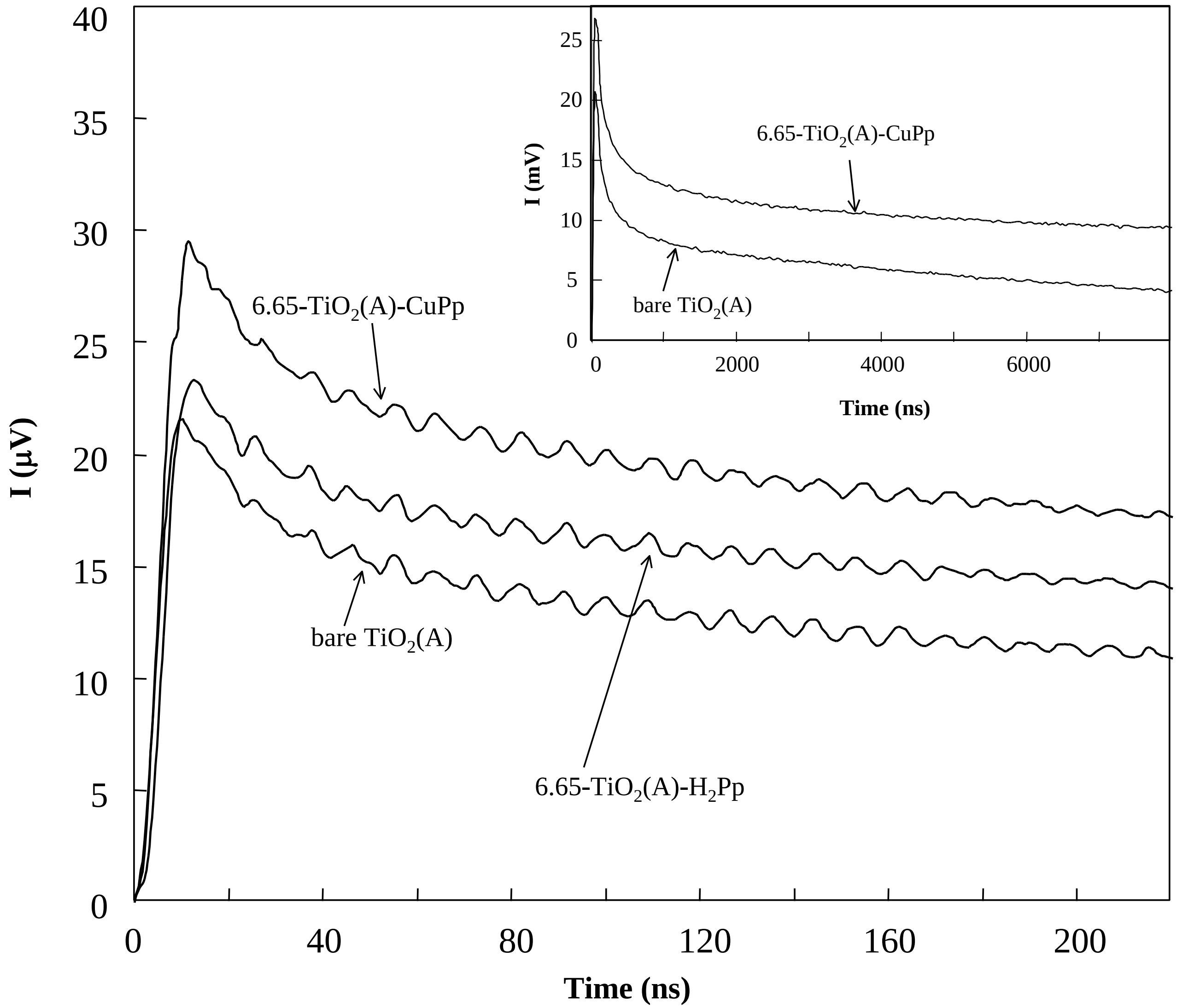


Figure 3. Time-resolved microwave conductivity (TRMC) experiments for bare TiO_2(A); 6.65-TiO_2(A)-H_2Pp and 6.65- TiO_2(A)-CuPp. Inset: bare TiO_2 (A) and 6.65-TiO_2(A)-CuPp.

Role of electrons

$$^{3}O_2 + e^-_{CB} \rightarrow {}^{\cdot}O_2^-$$

$$^{1}O_2(^{1}\Delta) + e^-_{CB} \rightarrow {}^{\cdot}O_2^-$$

$$H_2O_2 + e^-_{CB} \rightarrow {}^{\cdot}OH + OH^-$$

$$TiO_2[Cu(II)Sens] + e^-_{CB} \rightarrow TiO_2[Cu(I)Sens]$$

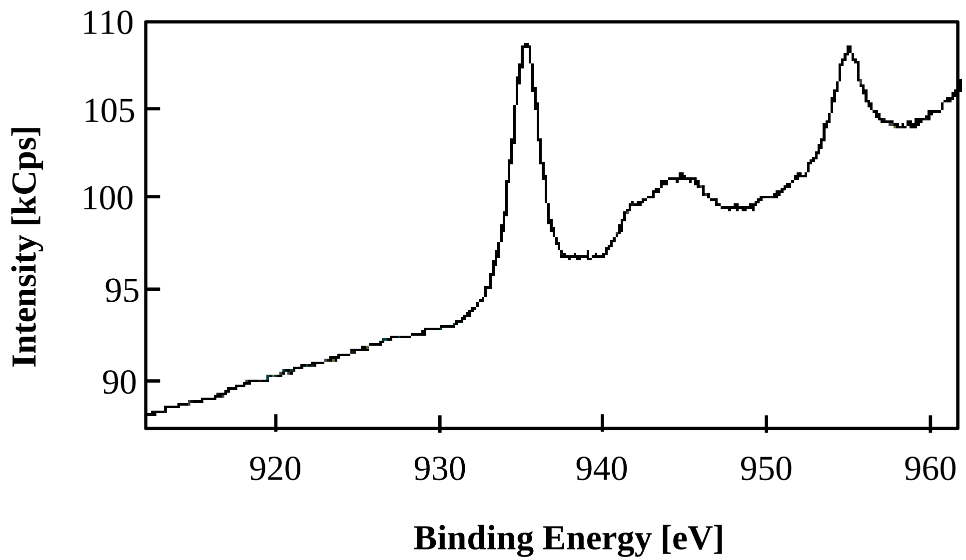


Figure 4. High-resolution XP spectrum of Cu2p region recorded on TiO_2(A)-CuPp (the spectrum has been subtracted of source satellites).

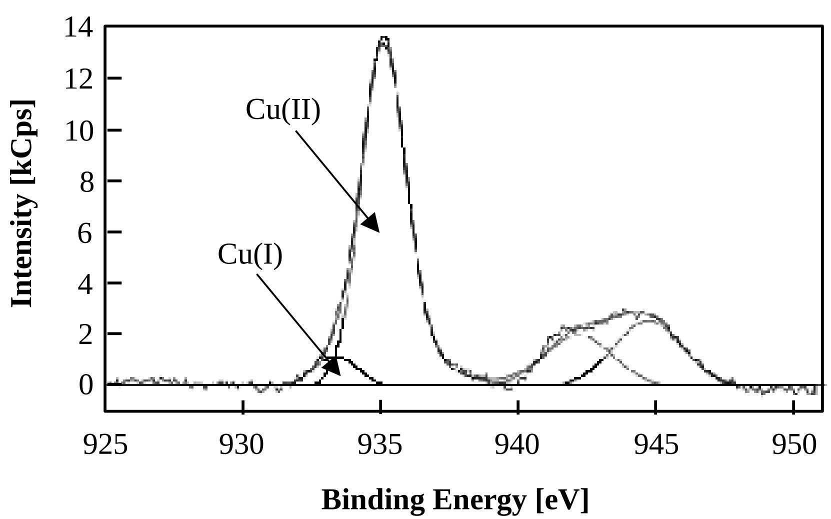


Figure 5. The Cu2p curve-fitted region of the TiO_2(A)-CuPp.

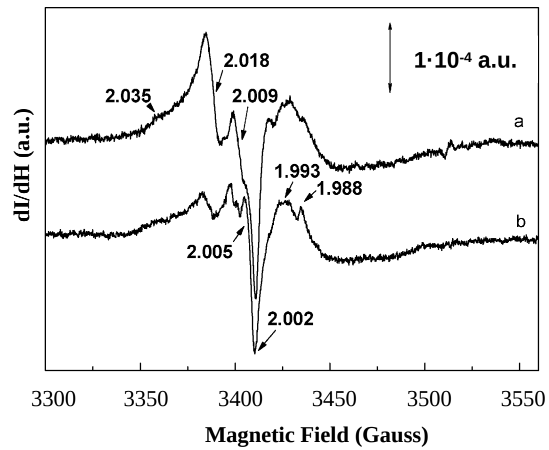


Figure 6. EPR spectra of the samples a) TiO_2(A) and b) 6.65-TiO_2(A)-H_2Pp, UV-irradiated in the presence of O_2 at 77 K. The background spectrum of each sample recorded in vacuum was subtracted.

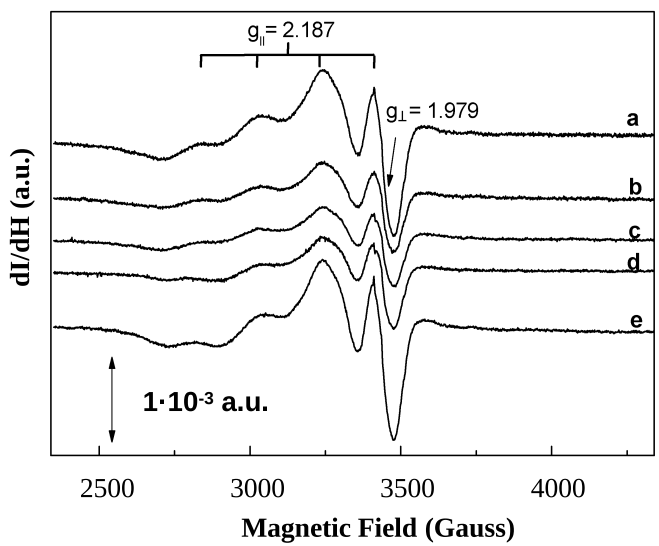


Figure 7. EPR spectra of the samples 6.65-TiO_2(A)-CuPp a) outgassed 1h at RT, b) UV-irradiated at 77 K, c) contacted with O_2 and d) irradiated at the same temperature and e) warmed at RT.

Role of holes

$$OH^- + h^+_{VB} \rightarrow {}^{\cdot}OH$$

$$H_2O + h^+_{VB} \rightarrow {}^{\cdot}OH + H^+$$

$$H_2O_2 + h^+_{VB} \rightarrow HO_2^{\cdot} + H^+$$

$$HO_2^{\cdot} + h^+_{VB} \rightarrow O_2 + H^+$$

$$TiO_2[MSens] + h^+_{VB} \rightarrow TiO_2[MSens]^+$$

Role of the sensitizer

intersystem crossing

$$[MSens] \xrightarrow{h\nu} {}^{1}[MSens]^{*} \xrightarrow{(isc)} {}^{3}[MSens]^{*}$$

$${}^{3}[MSens]^{*} + {}^{3}O_2 \rightarrow [MSens] + {}^{1}O_2({}^{1}\Delta)$$

$${}^{3}[MSens]^{*} + {}^{3}O_2 \rightarrow [MSens]^{+} + {}^{\cdot}O_2^{-}$$

$$TiO_2\ {}^{3\text{ or }1}[MSens]^{*} \rightarrow TiO_2[MSens]^{+} + e^{-}_{CB}$$

$$TiO_2[MSens]^{+} + OH^{-} \rightarrow TiO_2[MSens] + {}^{\cdot}OH$$

$$TiO_2[MSens]^{+} + \text{4-NP} \rightarrow TiO_2[MSens] + \text{oxidation products}$$

Role of some reactive intermediates in aqueous phase

$^{\cdot}O_2^{-} + H_2O \rightarrow HO_2^{\cdot} + OH^{-}$

$^{\cdot}O_2^{-} + H^{+} \rightarrow HO_2^{\cdot}$

$2HO^{\cdot} \rightarrow H_2O_2$

$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2$

$H_2O_2 + {}^{\cdot}O_2^{-} \rightarrow HO^{\cdot} + OH^{-} + O_2$

$2HO_2^{\cdot} + {}^{\cdot}O_2^{-} \rightarrow HO^{\cdot} + OH^{-} + 2O_2$

Role of metal

$$TiO_2[Cu(I)Sens] \quad + \quad {}^3O_2 \quad \rightarrow \quad TiO_2[Cu(II)Sens] \quad + \quad {}^{\cdot}O_2^{-}$$

$$TiO_2[Cu(I)Sens] \quad + \quad {}^1O_2({}^1\Delta) \quad \rightarrow \quad TiO_2[Cu(II)Sens] \quad + \quad {}^{\cdot}O_2^{-}$$

$$TiO_2[Cu(I)Sens] \quad + \quad H_2O_2 \quad \rightarrow \quad TiO_2[Cu(II)Sens] \quad + \quad HO^{\cdot} \quad + \quad OH^{-}$$

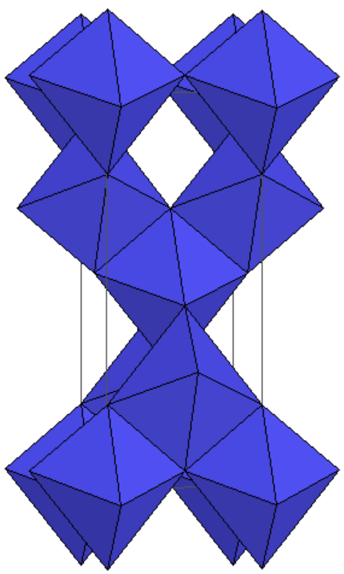
Oxidation reactions in aqueous phase

$^1O_2(^1\Delta)$ + 4-NP $\rightarrow$ oxidation products

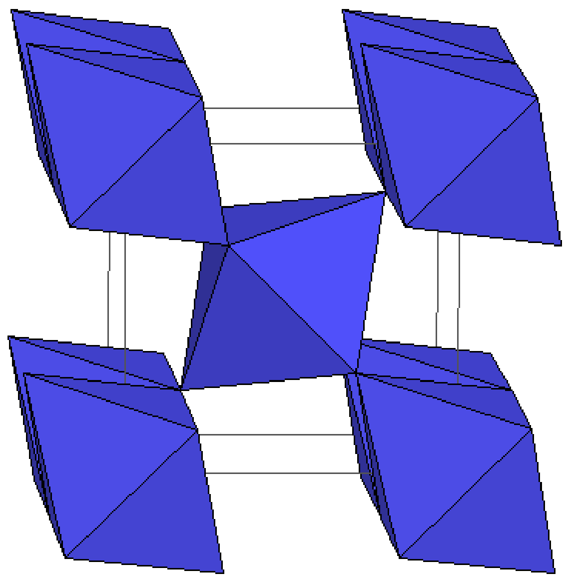
$HO_2^{\cdot}$ + 4-NP $\rightarrow$ oxidation products

$^{\cdot}HO$ + 4-NP $\rightarrow$ oxidation products

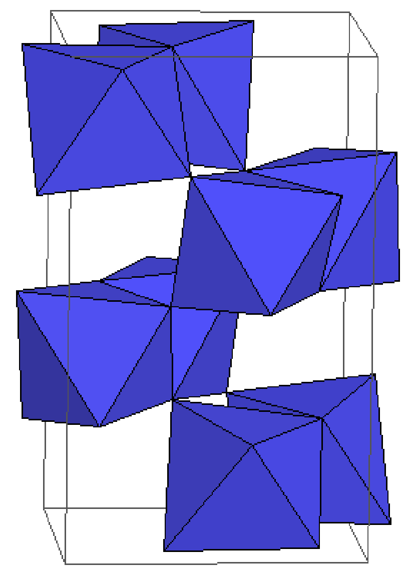
TiO_2 Structures



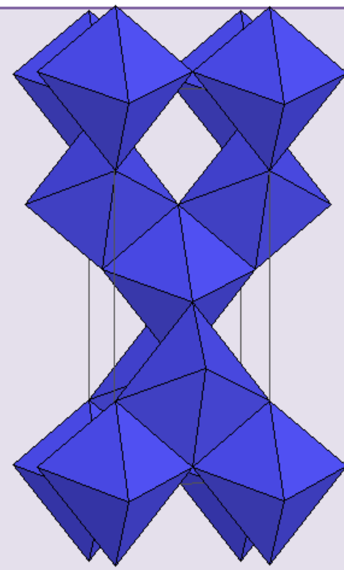
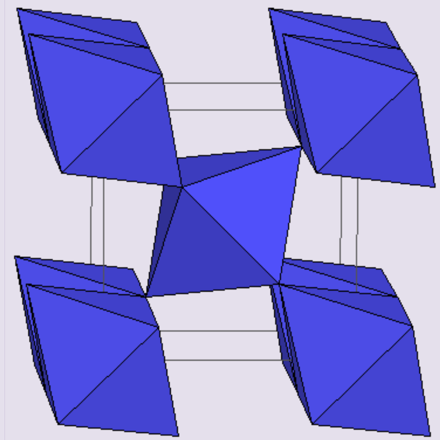
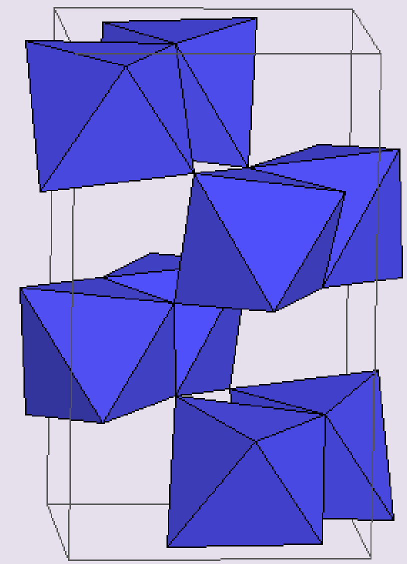
Anatse



Rutile



Brookite

Kind	Anatase	Rutile	Brookite
			
Crystal system	Tetragonal	Tetragonal	orthorhombic
Point Group	4/mmm	4/mmm	mmm
Space Group	$I4_1/amd$	$P4_2/mnm$	Pbca
Density	3.895	4.2743	4.123

TiO_2 as photocatalyst

ADVANTAGES

HIGH PHOTOACTIVITY

BIOLOGICAL AND CHEMICAL INERTNESS

PHOTOSTABILITY

LOW COST

NO TOSSIC

PHOTOCATALYTIC APPLICATION

BUILDINGS

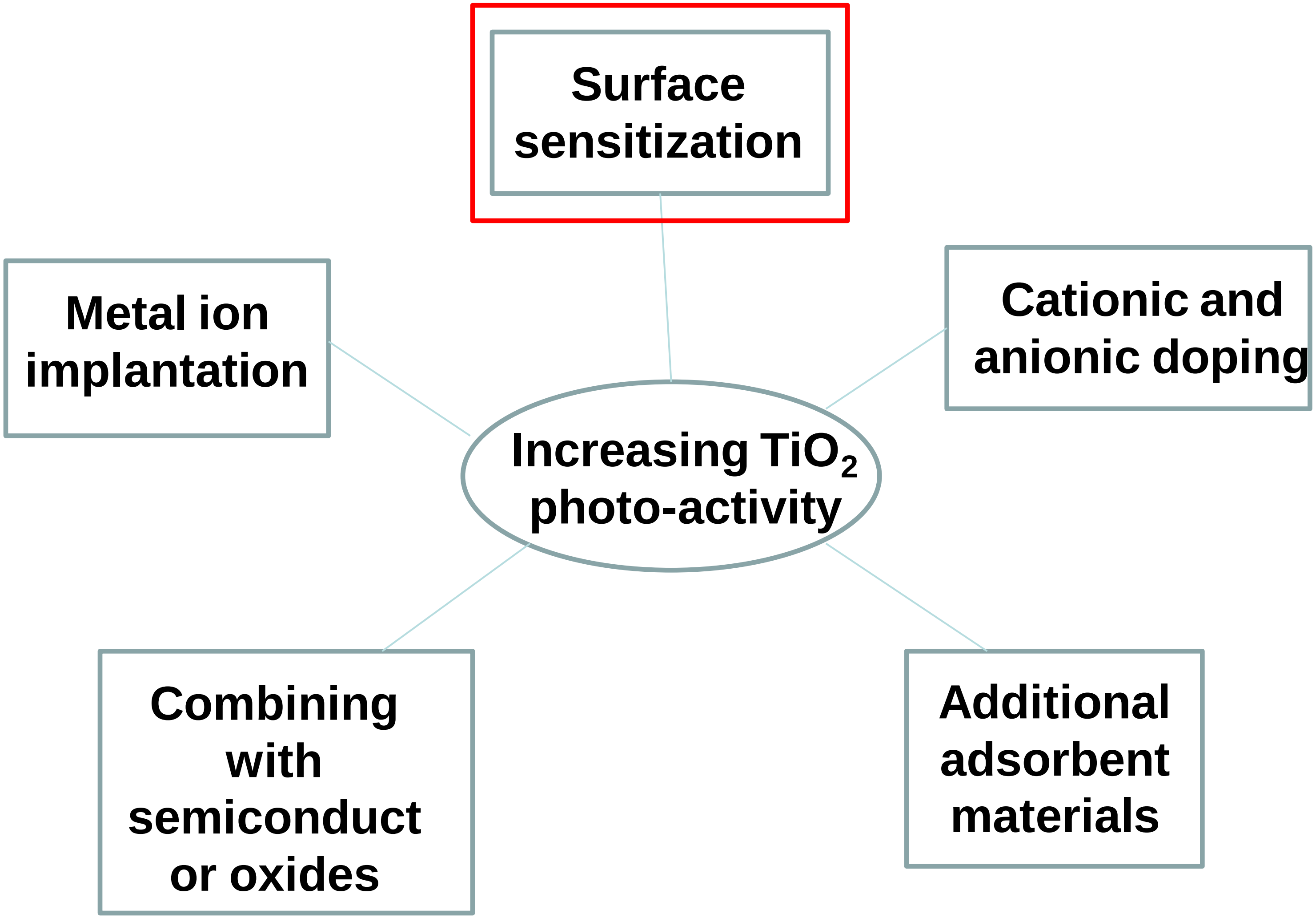
AIR PURIFICATION

WATER PURIFICATION

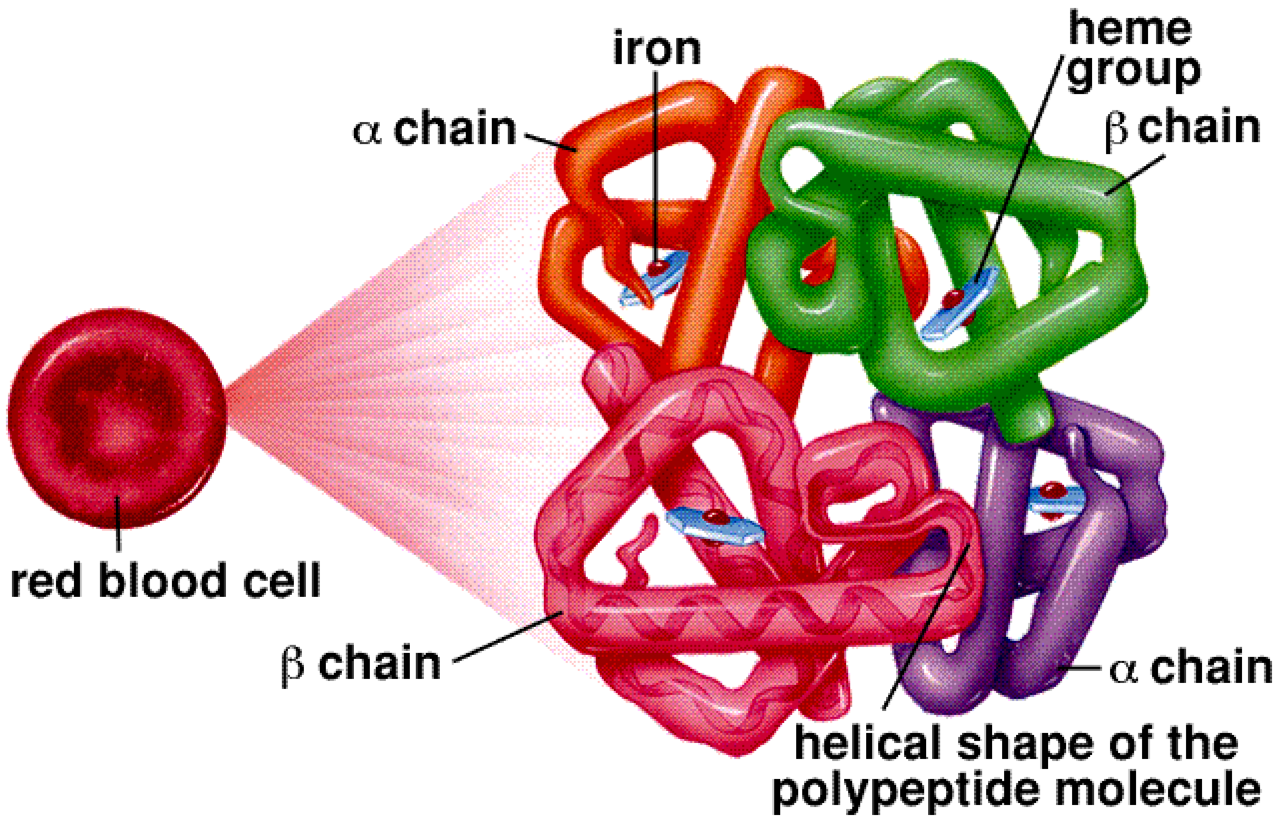
DISADVANTAGE

Works at λ < 400 nm (3-4% of solar radiation)

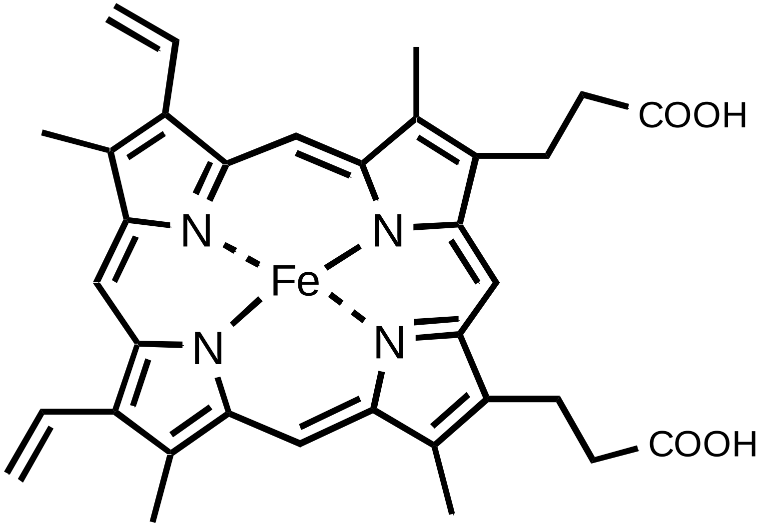
Techniques to improve TiO_2 photoactivity



Hemoglobin Molecule

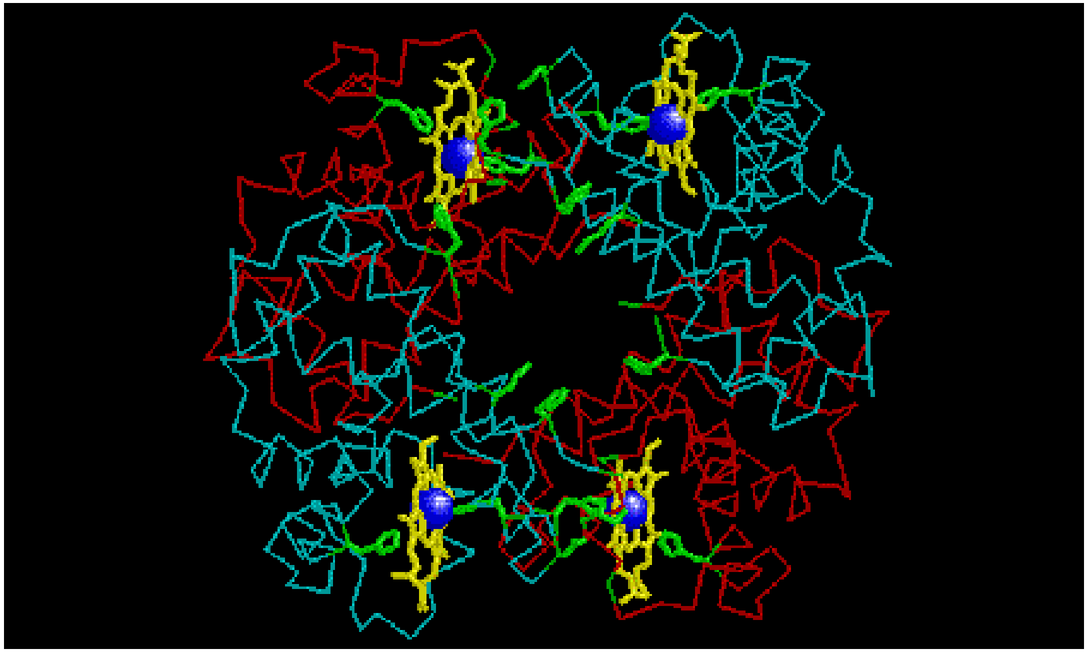


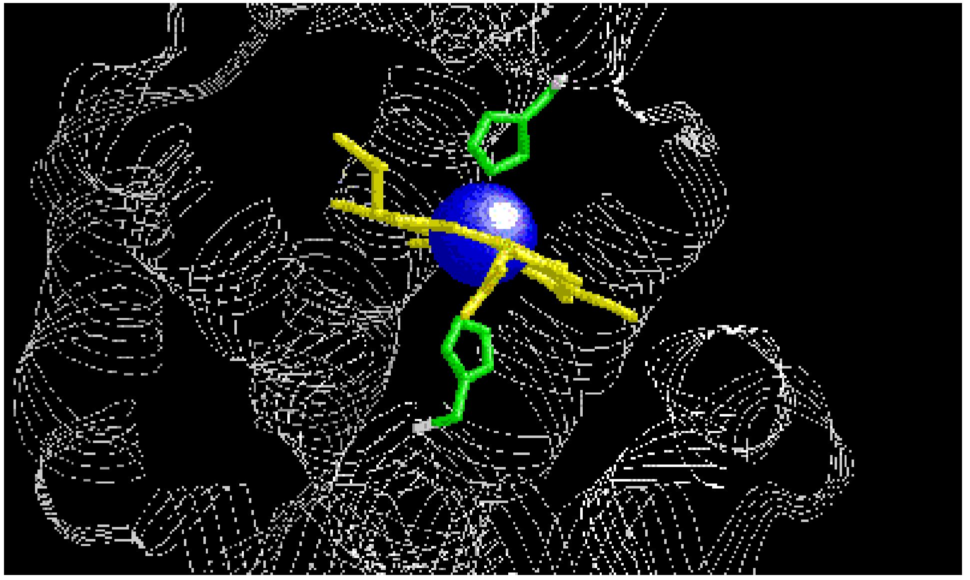
Biomimetic Catalyst



Hemin

Metallo-porphyrin having an iron ion located in the center.
Within the molecule, four nitrogen molecules hold the iron in the center.

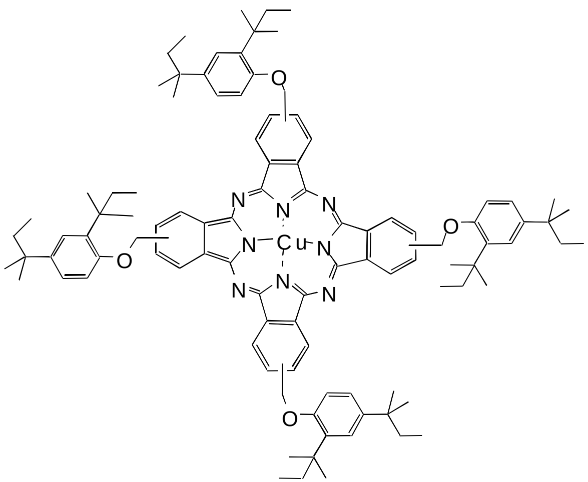




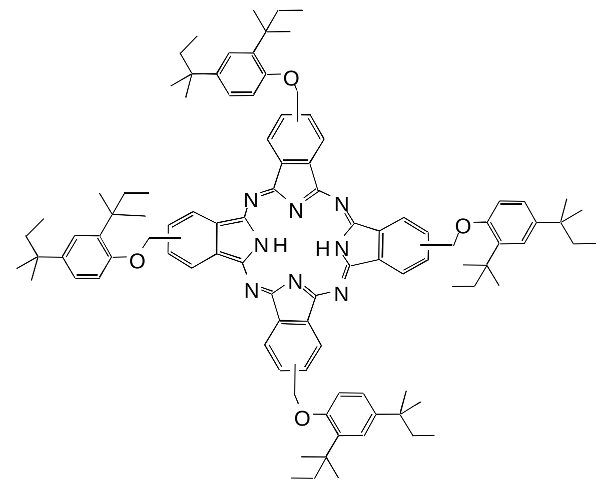
The iron ion also bonds with a histidine side chain from one of the subunits that form the pocket.

The iron ion bonds to histidine 87 in the alpha chain and histidine 92 in the beta chain. The histidine 87 and histidine 92 are both part of the F helix in each subunit.

Structure of Cu-Pc and H_2Pc



CuPc



H_2Pc

Cu(II)Tetrakis[4-(2,4-bis-(1,1-dimethyl)-propyl)-phenoxy)]phthalocyanine (CuPc)

Tetrakis[4-(2,4-bis-(1,1-dimethyl)-propyl)-phenoxy)]phthalocyanine (H_2Pc)

Mele et al. *Applied Catalysis B: Environmental* (2002) 38, 309.

Synthesis of Porphyrins Cardanol Based